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The research performed by the group at the Istituto di Struttura della Materia of the University of Messina, Italy, was:

1. Comparison of the experimental data on the scattering properties of aggregated spheres with the results of our calculations.
2. Study of the effect of clustering and correlation on the optical properties of intermediate and high-density dispersions of spherical particles within the framework of an enhanced version of the Bruggeman model.
3. Density dependence of the absorption coefficient, in the low and intermediate-density regime, for a dispersion of metal particles.

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The Optical properties of aerosols

Final Technical Report

by

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1 Introduction

The research performed by our group at the Istituto di Struttura della Materia of the Università di Messina, Italy, under the terms of Contract DAJA45-86-C0003 can be summarized as follows:

1. Comparison of the experimental data on the scattering properties of aggregated spheres with the results of our calculations;
2. Study of the effect of clustering and correlation on the optical properties of intermediate and high-density dispersions of spherical particles within the framework of an enhanced version of the Bruggeman model.
3. Density dependence of the absorption coefficient, in the low and intermediate-density regime, for a dispersion of metal particles.

As a result of the research mentioned above a number of communications have been presented to International Conferences, one paper containing final results has been submitted to J. of the Optical Soc. Am. and a thesis for the graduation in physics has been submitted to the Faculty of Sciences of the University of Messina.

2 Comparison with experimental data

The programs we developed in the last ten years to calculate the properties of clustered spheres proved to be suitable to deal with a number of physically significant situations. Nevertheless, since we were asked in several instances how our results compare with the experimental data, we determined to assess the reliability of our calculations through direct comparison with the data for single clusters published by Schuermann and Wang. These authors in fact performed a series of measurements of the forward-scattering amplitudes of single clusters composed of 2, 4 and 8 spheres both with real and with complex refractive index as a function either of the angle of incidence of the incoming plane wave or of the separation of the components. The measurements were actually performed in the microwave range on dielectric spheres with size parameter ranging from 3 to 8.

Thanks to the flexibility of our programs we were able to reproduce the measurements within the experimental error, that according to the statement of the authors is of the order of 10 % in magnitude and 12° in phase. Furthermore, thank to our analysis of the transformation properties of the forward -scattering amplitude under changes of the direction of

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in incidence we are able to justify, on theoretical grounds, the shape of the curves reported by Schuermann and Wang.

The preliminary results of our calculations formed the subject of a Communication to be published in the Proceedings of the European Aerosol Conference, held in Vienna, Austria, on September 18-23, 1989.

3 Influence of clustering and correlation

The optical and dielectric behavior of high-density dispersions of scatterers is commonly dealt with within the framework of the *Effective Medium Theory* using either the Bruggeman or the Maxwell-Garnett model. Unfortunately, both these models were developed in the dipole approximation, *i. e.* neglecting the effect of the higher multipoles and in particular of the magnetic dipole. Although in recent times the *Effective Medium Theory* was modified to deal with phenomena definitely attributable to magnetic-dipole effects, even the most recent improvements are not applicable but to particles with very small size-parameter.

To improve on this point and to overcome the limitations of the theory due to the complete lack of interparticle correlation in the distribution we propose some modifications to the original mixing rule of Bruggeman. The first improvement is to use the full Mie expansion to describe the scattering properties of single particles: this allows us to deal with scatterers with size-parameters up to 1.

As a second improvement we introduced into a distribution of dielectric and metal particles a correlation of exclusion designed to prevent contact among the metallic one. This effect is achieved by putting around each particle a thin dielectric layer with $\epsilon = 1$. Then, by gradually increasing the thickness of the exclusion layer we were able to follow the transition from a behavior typical of the Bruggeman model to one more appropriate to the Maxwell-Garnett model.

As a final improvement we included into our calculations the possibility that the particles aggregate in pairs thus forming anisotropic scatterers either all oriented alike or at random.

The results we got can be summarized as follows. The effective Medium Theory cannot be applied to media composed of particles with size-parameters of the order unity: our calculation show that a size-parameter of the order 0.1 is a practical limit for the reliability of the theory. Furthermore, the clustering may have visible effects on the percolation threshold of a dispersion of metal spheres, specially when the clusters are allowed to orient all alike. Finally the introduction of the correlation of exclusion produces a rather sharp

transition from the Bruggeman model to the Maxwell-Garnett model. Nevertheless the transition is not so sharp as to prevent us from following the change of the behavior of the dispersion.

The calculations summarized above form the subject of a Communication to the 2d Int. Conf. on Optical Particles Sizing held in Phoenix, Arizona, 4-7 march, 1990. A complete paper including all our results has been submitted to J. Optical Soc. Am.

4 Density dependence of the absorption coefficient

The problem of the density dependence of the absorption coefficient of a dispersion of particles is of paramount importance both from the theoretical and from the experimental point of view. It is well known, indeed, that one often speaks of *low-density* or of *high-density* dispersions, but on the precise definitions of these terms there exist only some rule of thumb based on the knowledge gained from experiments. For this reason we put Mr Fucile, one of our undergraduate students, in charge of a research aimed at developing a suitable method to determine the density dependence of then absorption coefficient of a dispersion of spherical particles, as part of a graduation thesis to be submitted to the Faculty of Sciences of our University.

The method used by Mr Fucile is based on the fact that the density dependence of the optical properties of a dispersion is due to the progressive increase of the multiple scattering effects and that effects of this kind are fully accounted for by the method we used till now to deal with clusters of spheres. Therefore the dispersion was considered as composed of pairs of spherical scatterers. The properties of each pair were calculated through our usual method including the analytic average over the orientations. The product of this calculation is the average forward-scattering amplitude of a pair which still depends, however, on the separation of the component spheres. At this stage we take advantage of the results of statistical physics to set up the *pair correlation function* appropriate for the density under consideration and to use it to perform an average over the separation of the particles. As a result we get an effective spherical scatterer *dressed* by the effects due to the presence, in the dispersion, of other particles. At this stage the calculation of the optical properties of the dispersion is only a matter of using well known formulas.

As noted above, this research is the subject of a graduation thesis (in italian, of course), but we also extracted a preliminary Communication to the 3d Conference of the European Colloid and Interfaces Society to be held in Copanello, Italy, next September. We plan to submit a complete paper after the graduation of Mr Fucile.

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ANNEX

All the money received with the preceding payments has been spent to buy the hardware we need for our work.



AN ENHANCED BRUGGEMAN SCHEME AND THE PERCOLATION THRESHOLD OF A DISPERSION OF METAL PARTICLES

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1. INTRODUCTION

It is well known that the propagation of the electromagnetic waves through a composite can be studied by the *effective medium theory* provided that the particles be small enough with respect to the wavelength that a dielectric description of the composite as a whole is still meaningful^{1,2}. A possible way to deal with this problem is, indeed, to think of the macroscopic properties of a composite as a space average of its local properties and consequently to substitute the actual medium with an effective one. In practice the effective medium theory achieves this goal through the definition of a homogeneous medium capable of fitting the average propagation properties of the composite in such a way that, if this latter is embedded into the effective medium, no scattering is experienced^{1,2}. Unfortunately there is no universal recipe to build the dielectric constant of the effective medium, since the properties of a composite, depend on the nature, the shape and the size as well as on the concentration and on the possible correlation in the distribution of the constituent particles.

A particularly simple model composite medium, that in the framework of the effective medium theory leads to the so called Bruggeman mixing rule, is composed of spherical particles of very small size parameter with totally uncorrelated space distribution. If into the model above is forced enough correlation as to ensure that the particles are well separated and dispersed within a homogeneous matrix, one is lead, instead, to the Maxwell-Garnett mixing rule². Of course, apart from such a rough treatment of the correlation, the approximations of the two models above are rather severe as in actual composite media the size parameter of the particles is often not very small and the particles themselves may have a definitely nonspherical shape. In this respect the possibility of aggregation of several spherical particles should also be considered as this phenomenon produces effectively nonspherical scatterers³. Even by assuming that all the particles are actually spherical, their radii are seldom identical but are in general distributed within a more or less wide range. The literature reports several attempts to overcome at least some of these approximations: for instance, a dynamical extension of the Bruggeman rule applicable to size parameters up to 0.01 has been proposed by Stroud and Pan¹, while a similar extension of the Maxwell-Garnett rule and a distribution function for the radii have been introduced by Chýlek and Srivastava⁴.

In this paper we introduce a modified Bruggeman model to be applied when the size parameter of the particles is extended up to 0.1. Our extension is effected by describing the particles through the exact Mie amplitudes^{5,6} and including up to the quadrupole terms for the largest spheres. We tentatively considered also a medium composed of particles with size parameter up to ~ 1.0 by including terms up to the 2^{nd} -poles to ensure the convergency of our calculations. Nevertheless, we do not regard the results we obtained for this latter medium as reliable although they come out as a natural and smooth evolution of the results for spheres with smaller size. Indeed, we think that any attempt to describe the properties of a medium too coarsely grained with respect to the wavelength of the propagating radiation by the effective medium theory is bound to fail.

We apply our modified model to study also how the correlation affects the behavior of the percolation of a composite made of metal and of dielectric particles. The kind of correlation we forced onto this composite is a correlation of exclusion among the metal particles that we introduced within the framework of our Bruggeman-Mie model by putting around each metal sphere a very thin dielectric layer. Then, by increasing the thickness of the layer we are able to follow by our calculations the rather sharp decrease of the absorption that comes with the implied transformation of the topology from that of Bruggeman model to that of the Maxwell-Garnett one

2. THEORY.

The effective medium theory defines ϵ_{eff} as the dielectric constant of the homogeneous medium that can be substituted to the real medium without affecting the propagation of the electromagnetic waves. This is accomplished by requiring that ϵ_{eff} satisfies

the null scattering condition and is thus the solution to the equation

$$\sum_i N_i f_{\eta,i}(\epsilon_{\text{eff}}) = 0, \quad (1)$$

with

$$f_{\eta,i} = \hat{e}_\eta \cdot f_{\eta,i},$$

where \hat{e}_η is the polarization vector of the plane wave and $f_{\eta,i}$ is the normalized forward-scattering amplitude of any of the N_i identical particles of the i -th kind when immersed into the homogeneous effective medium of dielectric constant ϵ_{eff} .

According to Mie, the normalized forward-scattering amplitude of a homogeneous spherical particle with refractive index $n = \sqrt{\epsilon}$ embedded in a homogeneous medium of refractive index n_{ext} — in the present case $n_{\text{ext}} \equiv n_{\text{eff}} = \sqrt{\epsilon_{\text{eff}}}$ — is given by

$$f = -\frac{i}{4\pi k n_{\text{ext}}} \sum_{\ell m} W_{\ell m}^{(p)} A_{\ell m}^{(p)}, \quad (2)$$

where the polarization index η has been dropped for the sake of simplicity, $k = \omega/c$ and

$$A_{\ell m}^{(p)} = -R_{\ell}^{(p)} W_{\ell m}^{(p)}. \quad (3)$$

In eqs. (2) and (3) the $W_{\ell m}^{(p)}$'s are the multipole amplitudes of the incident plane wave, the $A_{\ell m}^{(p)}$'s are those of the scattered field and

$$R_{\ell}^{(p)} = \frac{(1 + \bar{\pi}\delta_{p1})U_{\ell}'u_{\ell} - (1 + \bar{\pi}\delta_{p2})U_{\ell}u_{\ell}'}{(1 + \bar{\pi}\delta_{p1})U_{\ell}'v_{\ell} - (1 + \bar{\pi}\delta_{p2})U_{\ell}v_{\ell}'} \quad (4)$$

with

$$u_{\ell} = y_{\text{ext}} j_{\ell}(y_{\text{ext}}), \quad v_{\ell} = y_{\text{ext}} h_{\ell}^{(1)}(y_{\text{ext}}), \quad U_{\ell} = y j_{\ell}(y), \quad \bar{\pi} = \frac{n}{n_{\text{ext}}} - 1, \quad y_{\text{ext}} = n_{\text{ext}} x, \quad y = nx.$$

$x = kp$ is the size parameter of the particle with radius p and p is a parity index that distinguishes the magnetic multipoles ($p = 1$) from the electric ones ($p = 2$). Accordingly, $R_{\ell}^{(1)}$ refers to the magnetic and $R_{\ell}^{(2)}$ to the electric 2^{ℓ} -pole. When $|y_{\text{ext}}| \ll 1$ eq. (4) can be expanded in terms of y_{ext} and one gets

$$R_1^{(2)} \simeq -\frac{2}{3} i y_{\text{ext}}^3 \frac{\epsilon - \epsilon_{\text{ext}}}{\epsilon - 2\epsilon_{\text{ext}}}, \quad R_1^{(1)} \simeq -\frac{i}{45} y_{\text{ext}}^5 \left(\frac{\epsilon}{\epsilon_{\text{ext}}} - 1 \right), \quad (5)$$

while the $R_{\ell}^{(p)}$'s for $\ell > 1$ are smaller. As a consequence, in the limit $x_i \rightarrow 0$, only the $R_1^{(2)}$'s as given in eq. (5) can be considered in eq. (1) and one obtains the well known Bruggeman mixing rule⁴

$$\sum_i V_i \frac{\epsilon_i - \epsilon_{\text{eff}}}{\epsilon_i + 2\epsilon_{\text{eff}}} = 0, \quad (6)$$

where $V_i = N_i v_i / V$ is the fraction of the total volume of the composite filled by the N_i spheres each of volume v_i , dielectric constant ϵ_i and size parameter x_i . In order to get a dynamical extension of the Bruggeman mixing rule, Stroud and Pan¹ do not neglect the $R_1^{(1)}$ term and thus include into the expansion of eq. (2) also the magnetic dipole term. Since they take $R_1^{(1)}$ and $R_1^{(2)}$ in the form of eq. (5), their mixing rule reads

$$\sum_i V_i \left[\frac{\epsilon_i - \epsilon_{\text{eff}}}{\epsilon_i + 2\epsilon_{\text{eff}}} + \frac{x_i^2}{30} (\epsilon_i - \epsilon_{\text{eff}}) \right] = 0 \quad (7)$$

and thus appears as an extension of eq. (6) to rather larger, although still small, sizes. The mixing rule of Chýlek and Srivastava⁴ lies on the very same approximations but these authors include size-dependent terms only when ϵ is very large — for instance, this is the case of metal spheres. They also include a size-distribution function $\lambda(\rho)$ and write

$$\sum_i V_i \frac{\epsilon_i - \epsilon_{\text{eff}}}{\epsilon_i - 2\epsilon_{\text{eff}}} + \sum_{j: |\epsilon_j| \gg 1} \frac{2\pi}{45} k^2 (\epsilon_j - \epsilon_{\text{eff}}) \int \rho^3 \lambda_j(\rho) d\rho = 0. \quad (8)$$

Obviously, the size-dependent terms in eq. (8) assume the same form they have in eq. (7) when $\lambda_j(\rho) = N_j \delta(\rho_j - \rho)$.

Since the only common implementations of eq. (1) are the zero-size approximation, eq. (6), and the small-size approximation, eqs. (7) and (8), we determined to test the reliability of the null scattering condition, eq. (1), when applied to larger particles. In practice, all the calculations we will present in the next section were performed by carrying to full convergence the exact Mie expansions to the effect of ensuring the inclusion of all significant contributions to the scattering amplitude, eq. (2). In this way we overcame all the limitations due to the small size of the particles but those that prevent the possibility of dealing with the whole medium through a dielectric description.

As mentioned in the preceding section, we also considered a model composite medium which, in a sense, is a hybrid between that of Bruggeman and that of Maxwell-Garnett; namely we calculated ϵ_{eff} for a dispersion of homogeneous dielectric spheres with $\epsilon = \epsilon_D$ and of spheres with a metal core, of dielectric constant ϵ_M , coated by a thin dielectric layer. The scattering properties of the coated spheres were not described through an approach based on the boundary conditions at the separation surface but rather by interposing between the core and the coating a very thin transition layer⁷ through which

$$\epsilon = \epsilon(r) = \epsilon_M + (3s^2 - 2s^3)\Delta$$

with

$$\Delta = \epsilon_D - \epsilon_M \quad \text{and} \quad s = \frac{r - \rho_M}{\rho_D - \rho_M},$$

where ρ_M is the radius of the metal core and ρ_D the inner radius of the dielectric coating. In this way we achieved a smooth transition between the two materials as the refractive index $n = n(r)$ is a regular function of r everywhere within the coated spheres. Consequently eq. (4) must be substituted by^{3,6}

$$R_\ell^{(p)} = \frac{G_\ell^{(p)'} u_\ell - (1 + \bar{n} \delta_{p2})^2 G_\ell^{(p)} u_\ell'}{G_\ell^{(p)'} v_\ell - (1 + \bar{n} \delta_{p2})^2 G_\ell^{(p)} v_\ell'} \quad (9)$$

where $G_\ell^{(p)} = G_\ell^{(p)}(x)$ are now calculated by numerical integration of the radial equations

$$\frac{d^2 G_\ell^{(p)}}{d\xi^2} - \frac{2}{n} \frac{dn}{d\xi} \frac{dG_\ell^{(p)}}{d\xi} \delta_{p2} + \left[n^2 - \frac{\ell(\ell+1)}{\xi^2} \right] G_\ell^{(p)} = 0$$

with $\xi = kr$. Of course, when the spheres are homogeneous, $\epsilon_D = \epsilon_M$ and eq. (9) reduces to eq. (4). As a matter of fact, all the calculations we will present in the next section were performed by using eq. (9), or eq. (4) when appropriate, with no approximation. It is also worth noticing that our previous calculations⁷ proved that the introduction of the transition layer, provided it is thin enough, has no influence on the results.

3. RESULTS AND DISCUSSION.

All the composite media we dealt with in our calculations are two-component ones; the first component is a dielectric with $\epsilon_D = 1$ and the second is a metal with

$$\epsilon_M = 1 - \frac{1}{\nu(\nu + i\gamma)} \quad (10)$$

where $\nu = \omega/\omega_p$, $\gamma = 1/(\tau\omega_p)$, viz. the dielectric material is the vacuum while the metallic component is described by the free-electron Drude constant⁹. This choice allows us an easy comparison with the preceding results of Stroud and Pan¹ and of Chýlek and Srivastava⁴. Anyway, we think that a greater sophistication of the description of the metallic component is of no usefulness within a framework substantially as naïve as the effective medium one.

If we assume the particles to be spherical, eq. (1) becomes

$$V_M f_M(\epsilon_{eff}) + (\rho_M/\rho_D)^3 (1 - V_M) f_D(\epsilon_{eff}) = 0, \quad (11)$$

where ρ_M is the radius of the metal spheres and ρ_D the radius of the dielectric ones, and the f 's are given by eqs. (2), (3) and (4).

When the metal spheres are coated by a dielectric layer we have

$$V_M f_{MC}(\epsilon_{eff}) + (\rho_M/\rho_D)^3 \{1 - V_M(1 + c_L)\} f_D(\epsilon_{eff}) = 0, \quad (12)$$

where f_{MC} refers to a sphere with a metal core of radius ρ_M and a dielectric coating layer with external radius

$$\rho_L = (1 + c_L)^{1/3} \rho_M.$$

and is thus given by eqs. (2), (3) and (9). The quantity c_L is defined as

$$c_L = v_L/v_M,$$

where v_L is the volume of the dielectric layer: in other words c_L gives the volume of the dielectric coating around each metal sphere as a fraction of the volume, v_M , of the metal spheres themselves. Of course

$$V_M \leq V_{M \max} = \frac{1}{1 + c_L}, \quad 0 \leq c_L \leq c_{L \max} = \frac{1}{V_M} - 1,$$

so that when $c_L = 0$, i.e. when the spheres have no coating, we get again the topology of the Bruggeman model, whereas, when $c_L = c_{L \max}$, we get the Maxwell-Garnett topology.

We calculated ϵ_{eff} according to eqs. (11) or (12) as a function of V_M for some values of $x_M = k\rho_M$ and of ν ; $\gamma = 0.01$ in all cases. In particular we report in figs. 1 and 2 $\text{Im}[\epsilon_{\text{eff}}]$ as calculated from eq. (11), and from the two-component implementations of eq. (6), of eq. (7) with $\rho_D = \rho_M$, and of eq. (8) with a δ -like distribution of the radii. Our main purpose is to show the most important features of the absorption of a composite medium at frequencies for which the metal component is by itself strongly absorbing. Therefore, we chose to plot our results for $\nu = 0.01$, Fig. 1, and for $\nu = 0.1$, Fig. 2, since, for many metals, these frequencies occur in the far and in the near infrared, respectively. It is worth noticing that both our eqs. (11) and (12) and their counterpart according to Stroud and Pan, eq. (7), show a dependence on the size of the dielectric spheres. When one assumes $\epsilon_D = 1$, i.e. when the dielectric is the vacuum, the problem arises whether its more or less minute subdivision into spherical cells may affect the results. As a matter of fact, we took $x_D = k\rho_D = 10^{-4}$ as our calculations evidence that the size of the vacuum spheres has very small influence either when their size is reduced to zero according to Chylek and Srivastava or when it is set equal to the size of the metal spheres according to Stroud and Pan. Indeed, the results are nearly indistinguishable for all the sizes of the metal spheres at which the implementations of the effective medium theory we deal with can be assumed to work correctly. The range of V_M both in Fig. 1 and in Fig. 2 has been chosen so as to show the influence of the size and of the frequency on the transition from a dielectric behavior to a metallic one. In fact, we think that $x_M = 0.1$ is an appropriate upper limit for the applicability of eq. (11), viz. it is a practical limit to the size of the grains of a composite medium in order that this latter, from the point of view of the dielectric properties, can be substituted by a homogeneous medium. Anyway, on the basis of our calculations we conclude that, for particles of size greater than 0.1 but rather smaller than 1, the form of $\text{Im}[\epsilon_{\text{eff}}]$ from eq. (11) is still meaningful both in the small- V_M region up to where the transition to the metallic behavior starts to appear and in the high- V_M region. In this connection we recall that eq. (6) should never be applied when $x > 0.01$ and that eqs. (7) and (8) cannot be thought of as accurate when $x_M \approx 0.1$, because these equations come out from a series expansion, eq. (5), of the exact Mie quantities, eq. (4). We notice that in Fig. 1 the curve for $x_M = 0.01$ is generated not only by our Bruggeman-Mie implementation, eq. (11), but also by the implementations of Stroud and Pan, eq. (7), and of Chylek and Srivastava, eq. (8); the curves from eqs. (7) and (8) for $x_M = 0.1$ do not appear in Fig. 1 for the approximations on which eqs. (7) and (8) are based result in solutions that are physically unacceptable. In fact, these equations, that are algebraic equations of the third degree, yield values of $\text{Im}[\epsilon_{\text{eff}}]$ that are either negative or everywhere vanishingly small or very large even in the low V_M region. In turn, in Fig. 2 the curves from eqs. (7) and (8) for $x_M = 0.1$ coincide with each other and are substantially different from that coming from eq. (11). Moreover, into the curve labelled (1), which refers to the results from our Bruggeman-Mie model for $x_M = 0.01$, coalesce the results from eqs. (7) and (8) for the same size as well as the results from the Bruggeman rule.

In Figs. 3 and 4 we plot $\text{Im}[\epsilon_{\text{eff}}]$ for $\nu = 0.01$ and for several values of c_L as calculated according to eq. (14); analogous results were obtained for $\nu = 0.1$. It is quite evident that the correlation of exclusion produced by the dielectric coating around the metal spheres has very strong effects even at very low values of c_L . Actually, the model described in eq. (12) prevents any contact among the metal particles and is therefore topologically akin to the Maxwell-Garnett model. As a consequence, it is not surprising that, when c_L increases, our results tend very fast to those that are typical of the latter model. Figs. 3 and 4 show the results for $x_D = 10^{-4}$. At this value of x_D the contribution of the vacuum spheres to the scattering amplitude is very well approximated by the first of eqs. (5) and such a small size suggests the idea of a dielectric medium which pervades and fills all the space around the coated spheres. Actually, any size of the dielectric spheres up to $x_D = x_M$ proved to be incapable of affecting the results of our calculations from eq. (12). Of course, a more flexible model than that of eq. (12) can be built by introducing a distribution function for the thickness of the dielectric coating, including the possibility of zero thickness. Such a model would allow for contact among (only a fraction of) the metal spheres, so that an appropriate choice of the distribution function should ensure a smoother transition from the results of the Bruggeman model and those of the Maxwell-Garnett model.

The results we discussed above show that our Bruggeman-Mie approach yields meaningful results even when applied to particles with $x \approx 0.1$ and in this respect proves superior to the customary approaches, eqs. (6)–(8). In turn, our attempt to introduce some correlation among the metal particles, eqs. (12), proved too effective, perhaps. As remarked above, the amount of correlation we introduced into our models is so large that the results we reported can give only semiquantitative information, i.e. they can indicate the trend one has to expect in more realistic situations, that could be effectively simulated along the lines outlined above. As they stand, the models we presented in this paper can give, in our opinion, useful indications on the dielectric behavior of the composite media.

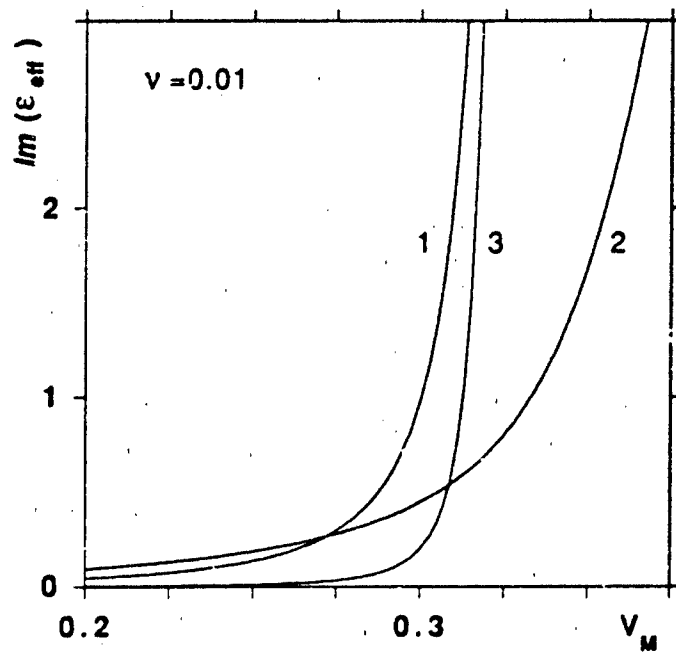


Fig. 1 - $\text{Im}(\epsilon_{\text{eff}})$ vs V_M from the Bruggeman-Mie model for $x=0.01$ (1) and $x=0.1$ (2); the results from the classical Bruggeman rule (3) are also reported.

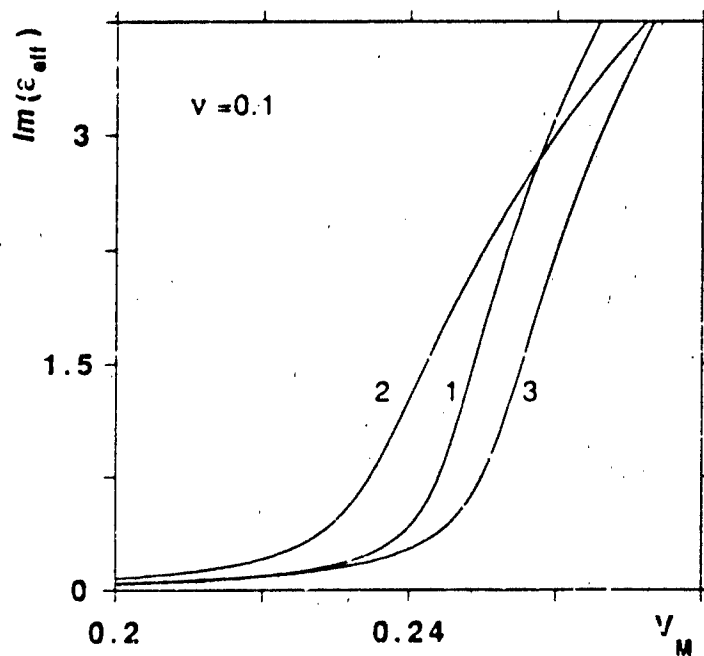


Fig. 2 - $\text{Im}(\epsilon_{\text{eff}})$ vs V_M from the Bruggeman-Mie model for $x=0.01$ (1) and $x=0.1$ (2); the results from the Stroud-Pan implementation (3) are also reported.

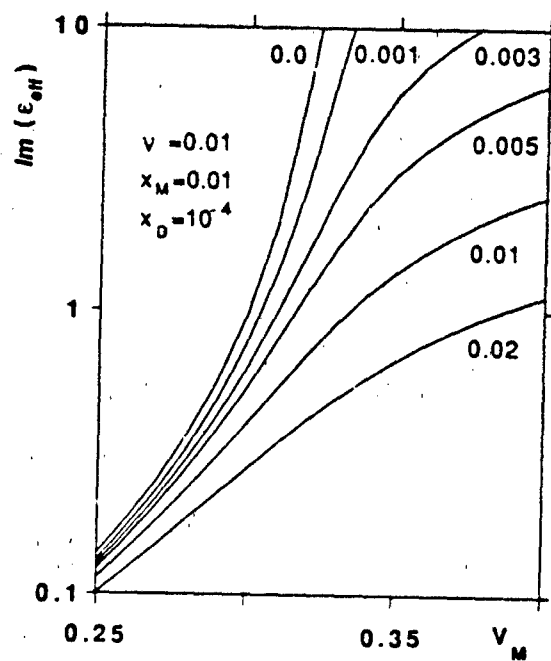


Fig. 3 - $\text{Im}(\epsilon_{\text{eff}})$ vs V_M from the coated sphere implementation. The curves are labelled by the corresponding value of c_L .

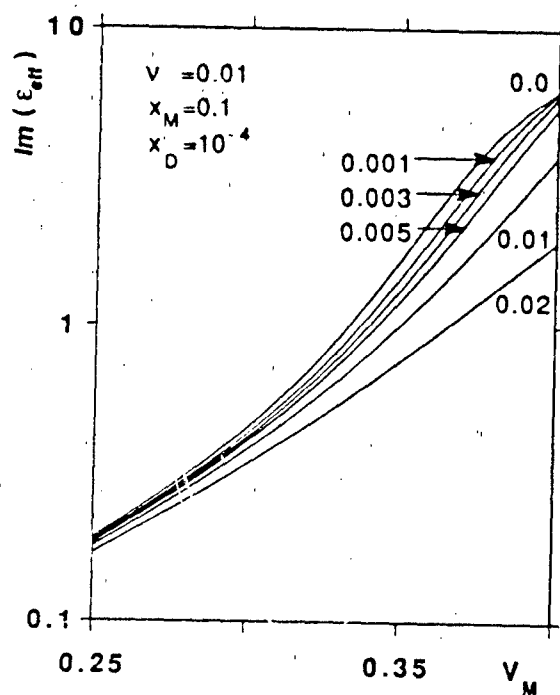


Fig. 4 - $\text{Im}(\epsilon_{\text{eff}})$ vs V_M from the coated sphere implementation. The curves are labelled by the corresponding value of c_L .

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Some enhancements to the Bruggeman mixing rule*

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Abstract

Some enhancements to the Bruggeman mixing rule designed to deal with composites made of particles of relatively large size, possibly correlated in their distribution, are proposed. The resulting implementations are applied to a composite made of metal and of dielectric spheres either uncorrelated or subject to a correlation of aggregation among the metal particles, or to a correlation of exclusion that prevents contact among the metal spheres. Our calculations show that our enhanced schemes work well up to sizes ≈ 0.1 and that both kinds of correlation above may have very strong effects on the transition of the composite from the dielectric to the metallic behavior.

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1 Introduction

In the last few years there has been an increase of interest in the propagation of electromagnetic waves through composite media in view of the practical relevance of several such materials [1,2,3]. A possible way to deal with this propagation problem is to think of the macroscopic properties of a composite as a space average of its local properties and consequently to substitute the actual medium with an effective one. In practice this is achieved, according to the *effective medium theory*, by building a homogeneous medium capable of fitting the average propagation properties of the composite in such a way that, if this latter is embedded into the effective medium, no scattering is experienced [4]. There is no universal recipe to build the dielectric constant of the effective medium, since the composites, by their very nature, may have the most diverse constitutions and topologies. In fact, the properties of a composite depend on the nature, the shape and the size as well as on the concentration and on the possible correlation in the distribution of the particles. A particularly simple model composite medium, that in the framework of the effective medium theory leads to the so called Bruggeman mixing rule, is composed of spherical particles of very small size parameter with totally uncorrelated space distribution. If into the model above is forced enough correlation as to ensure that the particles are well separated and dispersed within a homogeneous matrix [2], one is lead, instead, to the Maxwell-Garnett mixing rule. Of course, apart from such an extreme treatment of the correlation, which leads to so different topologies, the approximations of the two models above are rather severe. In actual composite media, indeed, the size parameter of the particles is often not very small and the particles themselves may have a definitely nonspherical shape. In this respect the possibility of aggregation of several spherical particles should also be considered as this phenomenon produces effectively nonspherical scatterers. Even by assuming that all the particles are actually spherical, their radii are seldom identical but are in general distributed within a more or less wide range. Of course some work has been done to overcome at least some of these approximations: for instance, a dynamical extension of the Bruggeman rule applicable to size parameters up to 0.01 has been proposed by Stroud and Pan [4], while a similar extension of the Maxwell-Garnett rule and a distribution function for the radii have been introduced by Chýlek and Srivastava [1].

In this paper we introduce a modified Bruggeman model to be applied when the size parameter of the particles is extended up to 0.1. Our extension is effected by describing the particles through the exact Mie amplitudes [5,6] and including up to the quadrupole terms for the biggest spheres. We tentatively considered also a medium composed of particles with size parameter up to ~ 1.0 by including terms up to the 2^4 -poles to ensure the convergency of our calculations. Nevertheless, we do not regard the results we obtained

for this latter medium as reliable although they come out as a natural and smooth evolution of the results for spheres with smaller size. Indeed, we think that any attempt to describe through the effective medium theory the properties of a medium too coarsely grained with respect to the wavelength of the propagating radiation is bound to fail.

We apply our modified model to study also the effect of the interparticle correlation on the behavior of the percolation of a composite made of metal and of dielectric particles. The first kind of correlation we forced onto the composite medium is a correlation of exclusion that we introduced within the framework of our Bruggeman-Mie model by putting around each metal sphere a very thin dielectric layer. Then, by increasing the thickness of the layer we are able to follow by our calculations the rather sharp decrease of the absorption that comes with the implied transformation of the topology from that of the Bruggeman model to that of the Maxwell-Garnett one.

When the metal particles of the composite are allowed to aggregate two other kinds of correlation set on: the one that produces the aggregation itself and the possible correlation in the orientations of the resulting anisotropic particles. We assess how the aggregation affects the dielectric behavior of the composite, at least for the simple case of binary aggregation, by performing some calculations through an approach we developed in the last few years. In fact, that approach describes the scattering by aggregates of spherical particles [7] through multipole amplitudes analogous to those of Mie as well as the macroscopic optical constants of a low-density dispersion of such aggregates either when they are oriented at random or alike [8]. Our results for the metal-dielectric composite referred to above show that the aggregation shifts the percolation towards lower concentrations of the metallic component when the aggregates are randomly oriented; when the aggregates are all oriented alike larger shifts occur with their magnitude depending on the direction of incidence and on the polarization of the propagating wave.

2 Theory

The effective medium theory defines ϵ_{eff} as the dielectric constant of the homogeneous medium that can be substituted to the real medium without affecting the propagation of the electromagnetic waves. This amounts to say that ϵ_{eff} should satisfy the *null scattering condition*, i.e. it is the solution to the equation

$$\sum_i N_i f_{\eta,i}(\epsilon_{\text{eff}}) = 0 \quad (1)$$

with

$$f_{\eta,i} = \hat{e}_\eta^* \cdot \mathbf{f}_{\eta,i}$$

where \hat{e}_η is the polarization vector of the plane wave and $f_{\eta,i}$ is the normalized forward-scattering amplitude of any of the N_i identical particles of the i -th kind when immersed into the homogeneous effective medium of dielectric constant ϵ_{eff} .

According to Mie, the normalized forward-scattering amplitude of a homogeneous spherical particle with refractive index $n = \epsilon^{1/2}$ embedded in a homogeneous medium of refractive index n_{ext} — in the present case $n_{\text{ext}} \equiv n_{\text{eff}} = \epsilon_{\text{eff}}^{1/2}$ — is given by

$$f = -\frac{i}{4\pi k n_{\text{ext}}} \sum_{\ell m} W_{\ell m}^{(p)*} A_{\ell m}^{(p)}, \quad (2)$$

where the polarization index η has been dropped for the sake of simplicity, $k = \omega/c$ and

$$A_{\ell m}^{(p)} = -R_{\ell}^{(p)} W_{\ell m}^{(p)}. \quad (3)$$

In eqs. (2) and (3) the $W_{\ell m}^{(p)}$'s are the multipole amplitudes of the incident plane wave, the $A_{\ell m}^{(p)}$'s are those of the scattered field and

$$R_{\ell}^{(p)} = \frac{(1 + \bar{n}\delta_{p1})U_{\ell}'u_{\ell} - (1 + \bar{n}\delta_{p2})U_{\ell}u_{\ell}'}{(1 + \bar{n}\delta_{p1})U_{\ell}'v_{\ell} - (1 + \bar{n}\delta_{p2})U_{\ell}v_{\ell}'} \quad (4)$$

with

$$u_{\ell} = y_{\text{ext}} j_{\ell}(y_{\text{ext}}), \quad v_{\ell} = y_{\text{ext}} h_{\ell}^{(1)}(y_{\text{ext}}), \quad U_{\ell} = y j_{\ell}(y),$$

$$\bar{n} = \frac{n}{n_{\text{ext}}} - 1, \quad y_{\text{ext}} = n_{\text{ext}} x, \quad y = nx.$$

$x = k\rho$ is the size parameter of the particle with radius ρ and p is a parity index that distinguishes the magnetic multipoles ($p = 1$) from the electric ones ($p = 2$). Accordingly, $R_{\ell}^{(1)}$ refers to the magnetic and $R_{\ell}^{(2)}$ to the electric 2^{ℓ} -pole. When $|y_{\text{ext}}| \ll 1$ eq. (4) can be expanded in terms of y_{ext} and one gets

$$R_1^{(2)} \simeq -\frac{2}{3} i y_{\text{ext}}^3 \frac{\epsilon - \epsilon_{\text{ext}}}{\epsilon + 2\epsilon_{\text{ext}}}, \quad R_1^{(1)} \simeq -\frac{i}{45} y_{\text{ext}}^5 \left(\frac{\epsilon}{\epsilon_{\text{ext}}} - 1 \right), \quad (5)$$

while the $R_{\ell}^{(p)}$'s for $\ell > 1$ are smaller. As a consequence, if one lets the size parameter x , of the particles involved in eq. (1) tend to zero, to obtain convergent values for the f_i 's, only the $R_1^{(2)}$'s as given in eq. (5) need be considered; then eq. (1) turns into the well known Bruggeman mixing rule [1]

$$\sum_i V_i \frac{\epsilon_i - \epsilon_{\text{eff}}}{\epsilon_i + 2\epsilon_{\text{eff}}} = 0, \quad (6)$$

where the x_i above is the size parameter of any of the N_i spheres of volume v_i and dielectric constant ϵ_i and $V_i = N_i v_i / V$ is the fraction of the total volume of the composite that such spheres fill. In order to get a dynamical extension of the Bruggeman mixing rule, Stroud and Pan [4] do not neglect the $R_1^{(1)}$ term and thus include into the expansion of eq. (2) also the magnetic dipole term. Since they take $R_1^{(1)}$ and $R_1^{(2)}$ in the form of eq. (5), their mixing rule reads

$$\sum_i V_i \left[\frac{\epsilon_i - \epsilon_{\text{eff}}}{\epsilon_i + 2\epsilon_{\text{eff}}} + \frac{x_i^2}{30} (\epsilon_i - \epsilon_{\text{eff}}) \right] = 0 \quad (7)$$

and appears as an extension of eq. (6) to rather larger, although still small, sizes. The mixing rule of Chýlek and Srivastava [1] lies on the very same approximations but these authors include the size dependent-terms above only when ϵ is very large — for instance, this is the case of metal spheres. They also include a size-distribution function $\lambda(\rho)$ and write

$$\sum_i V_i \frac{\epsilon_i - \epsilon_{\text{eff}}}{\epsilon_i + 2\epsilon_{\text{eff}}} + \sum_{j: |\epsilon_j| > 1} \frac{2\pi}{45} k^2 (\epsilon_j - \epsilon_{\text{eff}}) \int \rho^5 \lambda_j(\rho) d\rho = 0. \quad (8)$$

Obviously, the size-dependent terms in eq. (8) assume the same form they have in eq. (7) when $\lambda_j(\rho) = N_j \delta(\rho_j - \rho)$.

Since the only common implementations of eq. (1) are the zero-size approximation, eq. (6), and the small-size approximation, eqs. (7) and (8), we determined to test the reliability of the null scattering condition, eq. (1), when applied to larger particles. In practice, all the calculations we will present in the next section were performed by carrying to full convergency the exact Mie expansions to the effect of ensuring the inclusion of all significant contributions to the scattering amplitude, eq. (2). In this way we overcame all the limitations due to the small size of the particles but those that prevent the possibility of treating the whole medium through a dielectric description.

In section 1 we mentioned the special kind of correlation that sets on into the space distribution when the particles undergo aggregation phenomena. Here we will briefly describe how these cases can, in principle, be treated. Indeed, we presented elsewhere [7] a suitable approach to the scattering properties of an aggregation of spheres (cluster) designed to yield the forward scattering amplitude of the aggregate as a whole still in the form of eq. (2) but for that

$$A_{\ell m}^{(p)} = - \sum_{p'} \sum_{\ell' m'} S_{\ell m, \ell' m'}^{(p, p')} V_{\ell' m'}^{(p')}, \quad (9)$$

where the quantities $S_{\ell m, \ell' m'}^{(p, p')}$, defined in ref. [9], are analogous to the $R_\ell^{(p)}$'s, eq. (3), for the single spheres and take account of the specific geometry of the aggregation. If, as it

often occurs, we have to deal with a dispersion of randomly oriented identical aggregates and $f(\Theta)$ is the scattering amplitude of any one of them with orientation Θ , we can sum over all the orientations and get

$$\frac{N}{8\pi^2} \int f(\Theta) d\Theta = Nf,$$

where f on the right hand side is still in the form of eq. (2) but in this case

$$A_{\ell m}^{(p)} = -\frac{1}{2\ell+1} \sum_p \left[\sum_{m'} S_{\ell m' \ell m}^{(p,p')}(\Theta_0) \right] V_{\ell m}^{(p')}. \quad (10)$$

Thanks to the structure of the summation in eq. (10), the resulting A 's are independent of the particular orientation, Θ_0 , we chose to perform the calculation. The quantities S in eqs. (9) and (10) are the elements of a matrix that must be obtained by inversion of a square matrix of order $2\mathcal{N}L(L+2)$, defined in ref. [8], where \mathcal{N} is the number of the spheres in the aggregate and L is the value of ℓ at which the sums are truncated. Considerations on the symmetry of the aggregate, if any, can be used to factorize the matrix to be inverted [10,11]; in this respect, the most convenient case occurs when the centers of the spheres lie on a straight line, for the maximum order of the matrices to be inverted is $2\mathcal{N}L$ only. In the next section we will deal with binary aggregates with a truncation ℓ appropriate to the size of the spheres so that $L \leq 4$ has been sufficient in all cases and the computational effort has been therefore rather low.

As mentioned in the preceding section, we also considered a model composite medium which, in a sense, is a hybrid between that of Bruggeman and that of Maxwell-Garnett; namely we calculated ϵ_{eff} for a composite made of homogeneous dielectric spheres with $\epsilon = \epsilon_D$ and of spheres with a metal core, of dielectric constant ϵ_M , coated by a thin dielectric layer. The scattering properties of the coated spheres were not described through an approach based on the boundary conditions at the separation surface but rather by interposing between the core and the coating a very thin transition layer [9] through which

$$\epsilon = \epsilon(\tau) = \epsilon_M + (3s^2 - 2s^3)\Delta$$

with

$$\Delta = \epsilon_D - \epsilon_M \quad \text{and} \quad s = \frac{\tau - \rho_M}{\rho_D - \rho_M},$$

where ρ_M is the radius of the metal core and ρ_D the inner radius of the dielectric coating. In this way we achieved a smooth transition between the two materials as the refractive index

$n = n(r)$ is a regular function of r everywhere within the coated spheres. Consequently eq. (4) must be substituted by [12,6]

$$R_\ell^{(p)} = \frac{G_\ell^{(p)'} u_\ell - (1 + \bar{n} \delta_{p2})^2 G_\ell^{(p)} u_\ell'}{G_\ell^{(p)'} v_\ell - (1 + \bar{n} \delta_{p2})^2 G_\ell^{(p)} v_\ell'} \quad (11)$$

where $G_\ell^{(p)} = G_\ell^{(p)}(x)$ are now calculated by numerical integration of the radial equations

$$\frac{d^2 G_\ell^{(p)}}{d\xi^2} - \frac{2}{n} \frac{dn}{d\xi} \frac{dG_\ell^{(2)}}{d\xi} \delta_{p2} + \left[n^2 - \frac{\ell(\ell+1)}{\xi^2} \right] G_\ell^{(p)} = 0$$

with $\xi = kr$. Of course, when the spheres are homogeneous, $\epsilon_D = \epsilon_M$ and eq. (11) reduces to eq. (4). As a matter of fact, all the calculations we will present in the next section were performed by using eq. (11), or eq. (4) when appropriate, with no approximation. It is worth noticing that our previous calculations [9] proved that the introduction of the transition layer, provided it is thin enough, has no influence on the results.

3 Results and discussion

All the composite media we dealt with in our calculations are two-component ones; the first component is a dielectric with $\epsilon_D = 1$ and the second is a metal with

$$\epsilon_M = 1 - \frac{1}{\nu(\nu + i\gamma)}, \quad (12)$$

where $\nu = \omega/\omega_p$, $\gamma = 1/(\tau\omega_p)$, viz. the dielectric material is the vacuum while the metallic component is described by the free-electron Drude constant [13]. This choice allows us an easy comparison with the preceding results of Stroud and Pan [4] and of Chýlek and Srivastava [1]. Anyway, we think that a greater sophistication of the description of the metallic component is of no usefulness within a framework substantially as naïve as the effective medium one.

If we assume the particles to be spherical, eq. (1) becomes

$$V_M f_M(\epsilon_{\text{eff}}) + (\rho_M/\rho_D)^3 (1 - V_M) f_D(\epsilon_{\text{eff}}) = 0, \quad (13)$$

where ρ_M is the radius of the metal spheres and ρ_D the radius of the dielectric ones, and the f 's are given by eqs. (2), (3) and (4).

When the metal spheres are coated by a dielectric layer we have

$$V_M f_{MC}(\epsilon_{eff}) + (\rho_M/\rho_D)^3 [1 - V_M(1 + c_L)] f_D(\epsilon_{eff}) = 0, \quad (14)$$

where f_{MC} refers to a sphere with a metal core of radius ρ_M and a dielectric coating layer with external radius

$$\rho_L = (1 + c_L)^{1/3} \rho_M,$$

and is thus given by eqs. (2), (3) and (11). The quantity c_L is defined as

$$c_L = v_L/v_M$$

where v_L is the volume of the dielectric layer: in other words c_L gives the volume of the dielectric coating around each metal sphere as a fraction of the volume, v_M , of the metal spheres themselves. Of course

$$V_M \leq V_{M \max} = \frac{1}{1 + c_L}, \quad 0 \leq c_L \leq c_{L \max} = \frac{1}{V_M} - 1,$$

for a given c_L and for a given V_M , respectively, so that when $c_L = 0$, i.e. when the spheres have no coating, we get again the topology of the Bruggeman model, whereas, when $V_M = V_{M \max}$ or $c_L = c_{L \max}$ we get the Maxwell-Garnett topology.

When the spheres aggregate in pairs we have

$$V_M f_C(\epsilon_{eff}) + 2(\rho_M/\rho_D)^3 [1 - V_M] f_D(\epsilon_{eff}) = 0, \quad (15)$$

where f_C is the contribution of one aggregate averaged over the orientations as described in the preceding section.

It is perhaps worth noticing that eqs. (13)–(15), unlike the two-component implementations of eqs. (6)–(8), are transcendental equations in ϵ_{eff} , and thus require some further caution in seeking for their solutions.

We calculated ϵ_{eff} according to eqs. (13), (14) or (15) as a function of V_M for some values of $x_M = k\rho_M$ and of ν ; $\gamma = 0.01$ in all cases. In particular we report in figs. 1 and 2 $\text{Im}[\epsilon_{eff}]$ as calculated from eq. (13), and from the two-component implementations of eq. (6), of eq. (7) with $\rho_D = \rho_M$, and of eq. (8) with a δ -like distribution of the radii. Our main purpose is to show the most important features of the absorption of a composite medium at frequencies for which the metal component is by itself strongly absorbing. Therefore, we chose to plot our results for $\nu = 0.01$, Fig. 1, and for $\nu = 0.1$, Fig. 2, since, for many metals, these frequencies occur in the far and in the near infrared, respectively.

It is worth noticing that both our eqs. (13), (14) and (15) and their counterpart according to Stroud and Pan, eq. (7), show a dependence on the size of the dielectric spheres. When one assumes $\epsilon_D = 1$, i.e. when the dielectric is the vacuum, the problem arises whether its more or less minute subdivision into spherical cells may affect the results. As a matter of fact, we took $x_D = k\rho_D = 10^{-4}$ but our calculations confirm that the size of the vacuum spheres has very small influence either when their size is reduced to zero according to Chýlek and Srivastava or when it is set equal to the size of the metal spheres according to Stroud and Pan. As expected, our results are nearly independent of the size of the vacuum spheres, indeed, for all the sizes of the metal spheres at which the implementations of the effective medium theory we deal with can be assumed to work correctly. Of course this is true as far as ϵ_{eff} does not become so large within the range of V_M as to enhance the size-dependent contributions from the dielectric spheres. In practice, the range of V_M both in Fig. 1 and in Fig. 2 is not too large and yet it extends enough to show the influence of the size and of the frequency on the transition from a dielectric behavior to a metallic one. In our opinion $x_M = 0.1$ is an appropriate upper limit for the applicability of eq. (13), viz. it is a practical limit to the size of the grains of a composite medium in order that this latter, from the point of view of the dielectric properties, could be substituted by a homogeneous medium. Anyway, on the basis of our calculations we conclude that, for particles of size greater than 0.1 but rather smaller than 1, the form of $\text{Im}[\epsilon_{eff}]$ from eq. (13) is still meaningful in the small- V_M region. In this connection we recall that eq. (6) should never be applied when $x > 0.01$ and that eqs. (7) and (8) cannot be thought of as accurate when $x_M \simeq 0.1$, because these equations come out from a series expansion, eq. (5), of the exact Mie quantities, eq. (4). We notice that in Fig. 2 the curves for $x_M = 0.1$ from eqs. (7) and (8) coincide with each other and are substantially different from that coming from eq. (13), while they do not appear at all in Fig. 1 for the approximations on which eqs. (7) and (8) are based result in solutions that are physically unacceptable. In fact, these equations, that are algebraic equations of the third degree, yield values of $\text{Im}[\epsilon_{eff}]$ that are either negative or everywhere vanishingly small or very large even in the low V_M region.

In Figs. 3 and 4 we plot $\text{Im}[\epsilon_{eff}]$ for $\nu = 0.01$ and for several values of c_L as calculated according to eq. (14); analogous results were obtained for $\nu = 0.1$. It is quite evident that the correlation of exclusion produced by the dielectric coating around the metal spheres has very strong effects even at very low values of c_L . Actually, the model described in eq. (14) prevents any contact among the metal particles and is therefore topologically akin to the Maxwell-Garnett model. As a consequence, it is not surprising that, when c_L increases, our results tend very fast to those that are typical of the latter model. Figs. 3 and 4 show the results for $x_D = 10^{-4}$. At this value of x_D the contribution of the vacuum spheres to the scattering amplitude is very well approximated by the first of eqs. (5)

and such a small size suggests the idea of a dielectric medium which pervades and fills all the space around the coated spheres. Even in this case any size of the dielectric spheres up to $x_D = x_M$ proved to be incapable of affecting the results of our calculations from eq. (14). Of course, a more flexible model than that of eq. (14) can be built by introducing a distribution function for the thickness of the dielectric coating, including the possibility of zero thickness. Such a model would prevent the contact among (only a fraction of) the metal spheres, so that an appropriate choice of the distribution function should ensure a smoother transition from the results of the Bruggeman model and those of the Maxwell-Garnett model.

Figures 5 and 6, where $\text{Im}[\epsilon_{\text{eff}}]$ is plotted from eq. (15), for $\nu = 0.01$, show the effect of a complete binary aggregation of the metal particles on the transition of a composite medium to the metallic behavior; analogous results were obtained for $\nu = 0.1$. This kind of effect proves a quite significant one but it is very strongly increased when to the correlation of aggregation one also adds the request that all the binary aggregates be likely oriented. Even in this case the value of x_D proves to be irrelevant, although the conceptually most satisfactory choice is that of very small size (in practice $x_D = 10^{-4}$). Both Figures 5 and 6 show that the percolation undergoes a noticeable shift towards higher values of V_M when the common orientation of the aggregates is chosen so as their axes are parallel to the wavevector of the incident wave. This phenomenon is easily understandable if one thinks of the arrangement above as the one that provides the maximum of metal-free paths to the propagating radiation. On the other hand, the maximum in the extinction power of the medium that occurs when the axes of the aggregates are all parallel to the electric field can also be attributed to the arrangement, as this choice of the orientation maximizes the absorption of the individual aggregates. Of course, less strong effects should be expected if, more realistically, only a reasonable fraction of the metal particles were allowed to aggregate.

The results we discussed above show that our Bruggeman-Mie approach yields meaningful results even when applied to particles with $x \simeq 0.1$ and in this respect proves superior to the customary approaches, eqs. (6)–(8). In turn, our attempt to introduce some correlation among the metal particles, eqs. (14) and (15), proved too effective, perhaps. As remarked above, the amount of correlation we introduced into our models is so large that the results we reported can give only semiquantitative information, *i.e.* they can indicate the trend one has to expect in the more realistic situations that could be effectively simulated along the lines outlined above. As they stand, the models we presented in this paper can give, in our opinion, useful indications on the dielectric behavior of the composite media.

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Figure captions

Figure 1 : $\text{Im}[\epsilon_{\text{eff}}]$ vs. V_M , from eq. (13) for $\nu = 0.01$ and $x_D = 10^{-4}$. The results from eqs. (6)–(8) are also reported for the sake of comparison. The label B denotes the curve from eq. (6); as, on this scale, several curves are undistinguishable from each other the labels give x_M and the number of the equations that generate the curve.

Figure 2 : Same as Fig. 1 but for $\nu = 0.1$.

Figure 3 : $\text{Im}[\epsilon_{\text{eff}}]$ vs. V_M , from eq. (14), calculated for the values of c_L that label the curves. $x_M = 0.01$, $x_D = 10^{-4}$ and $\nu = 0.01$.

Figure 4 : Same as Fig. 3 but for $x_M = 0.1$.

Figure 5 : $\text{Im}[\epsilon_{\text{eff}}]$ vs. V_M , from eq. (15), for binary aggregates with $x_M = 0.01$, $x_D = 10^{-4}$ and $\nu = 0.01$. The unlabelled solid curve refers to randomly oriented aggregates; that labelled \parallel refers to aggregates all oriented with their axes parallel to the wavevector and the one labelled \perp refers to aggregates with their axes parallel to the electric field of the wave which is assumed to be linearly polarized. The dashed curve reports, for the sake of comparison, the results from eq. (13).

Figure 6 : Same as Fig. 5 but for $x_M = 0.1$.

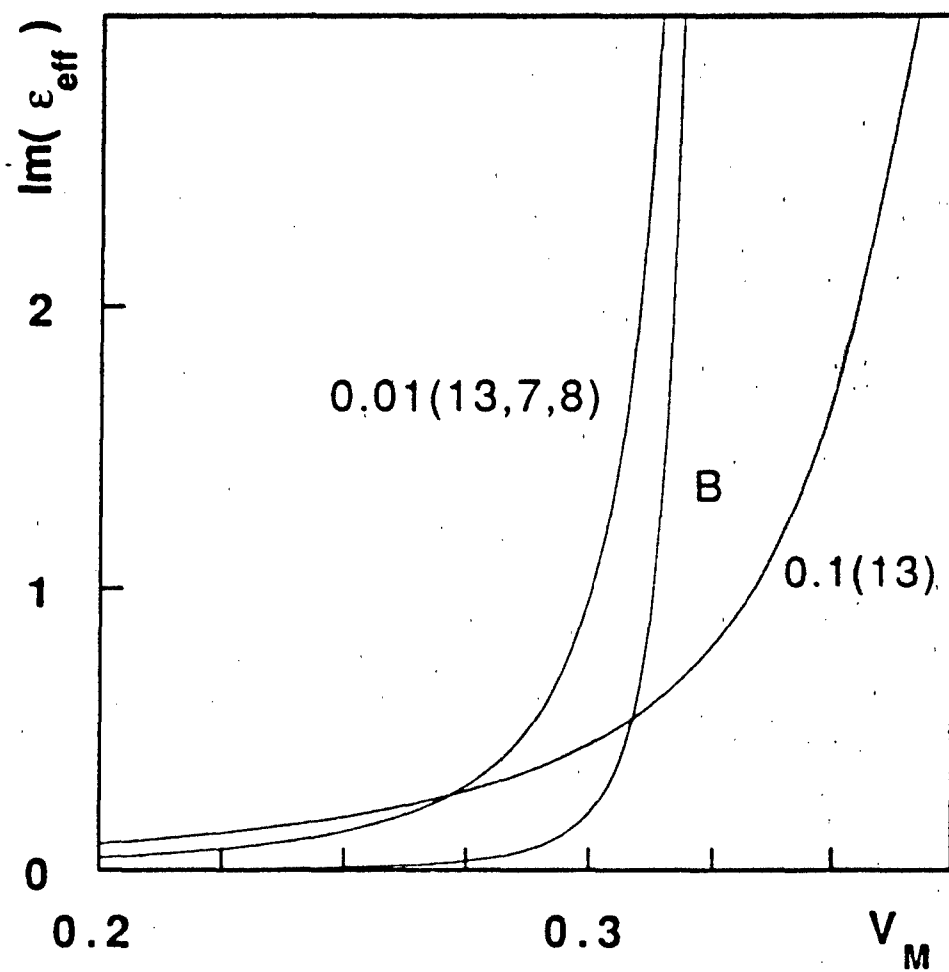
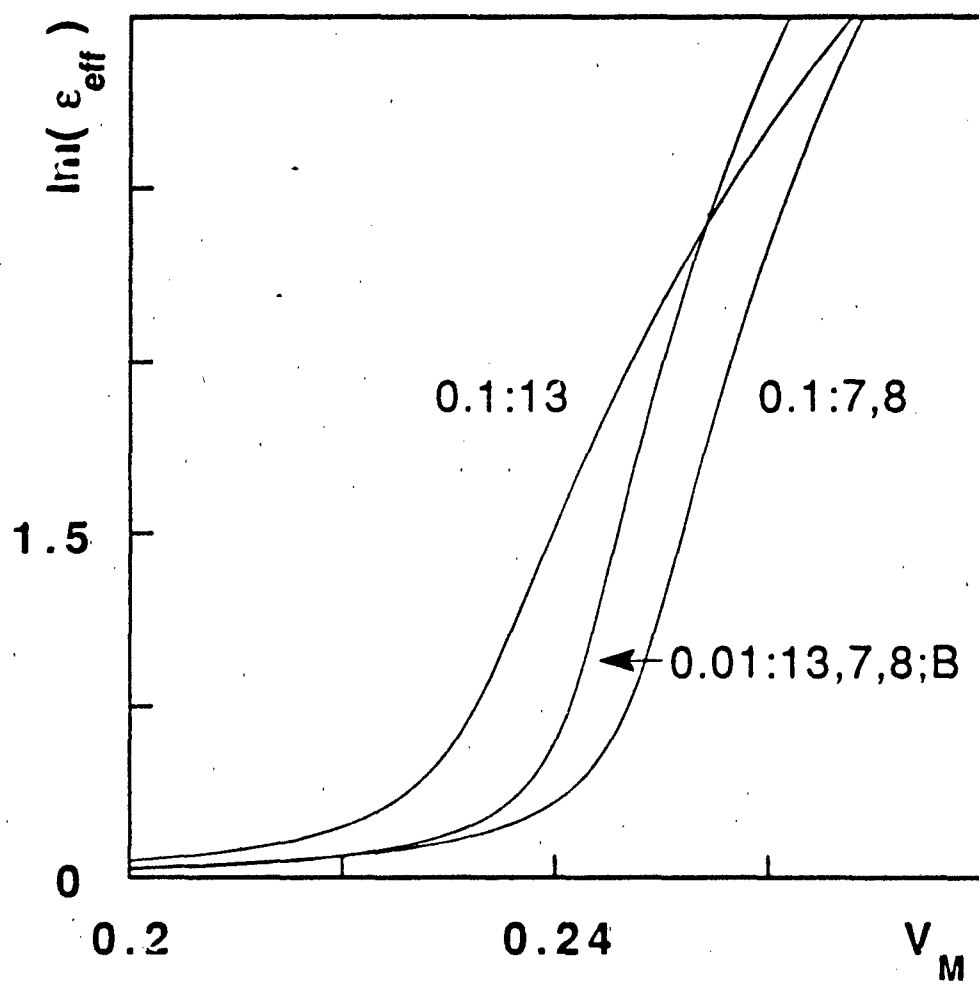
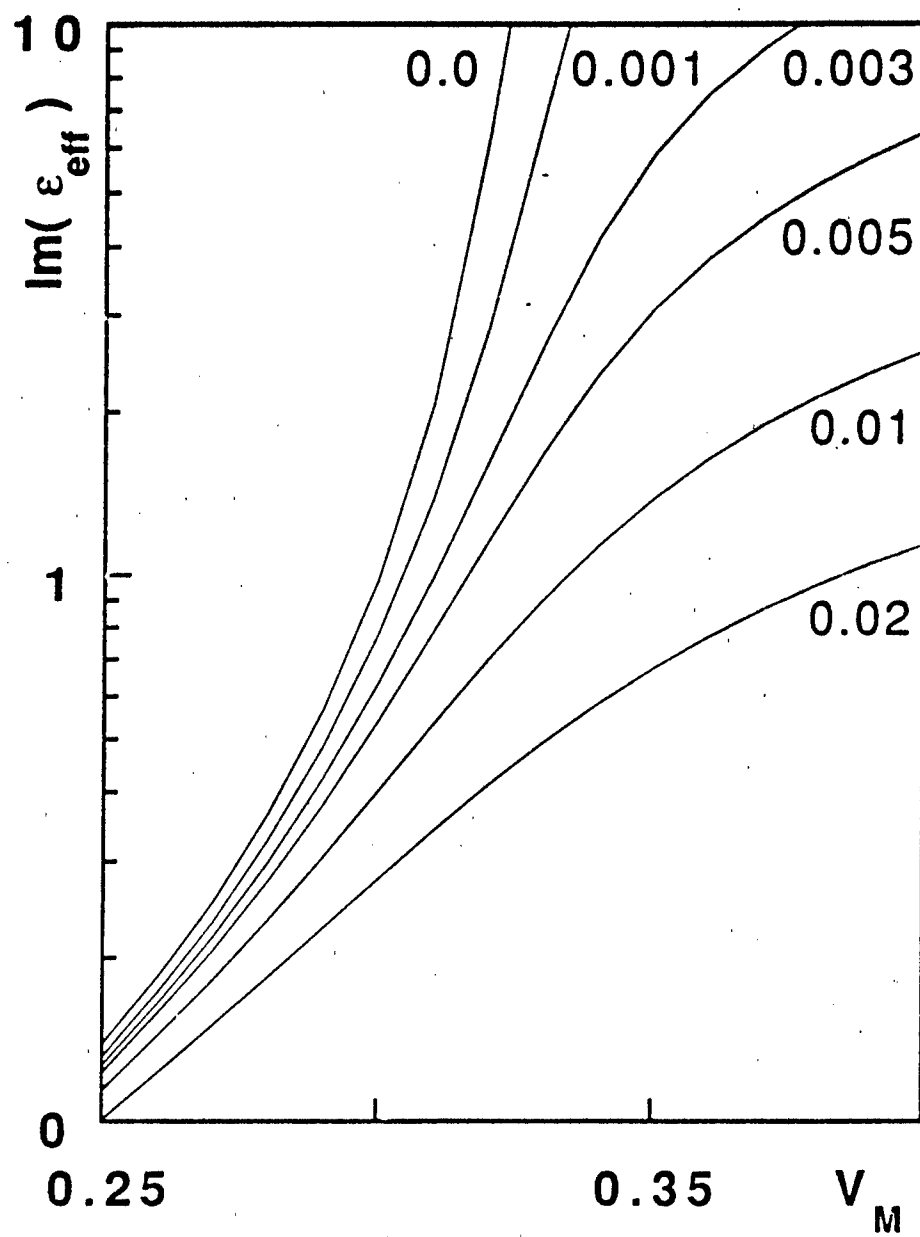
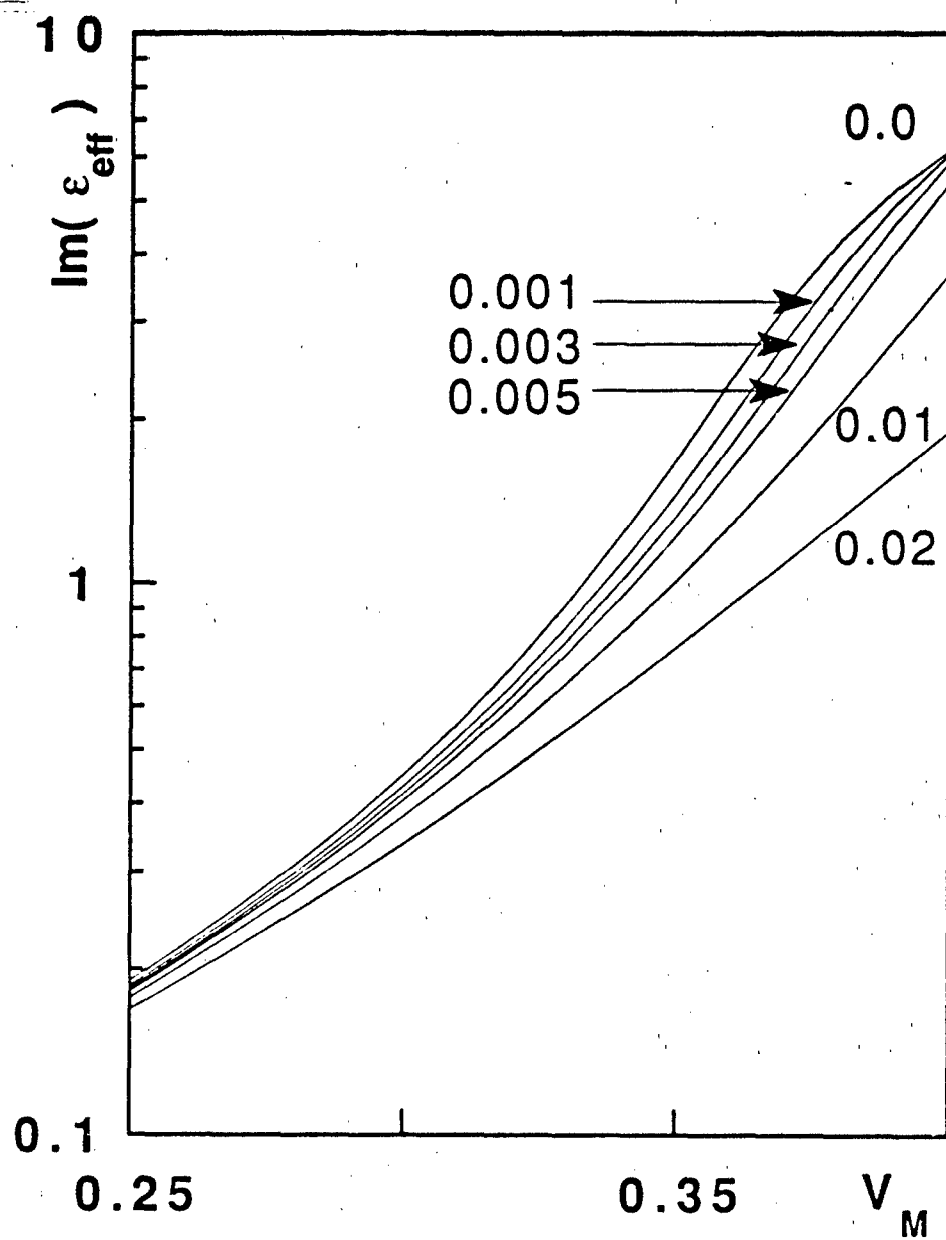


FIG. 1







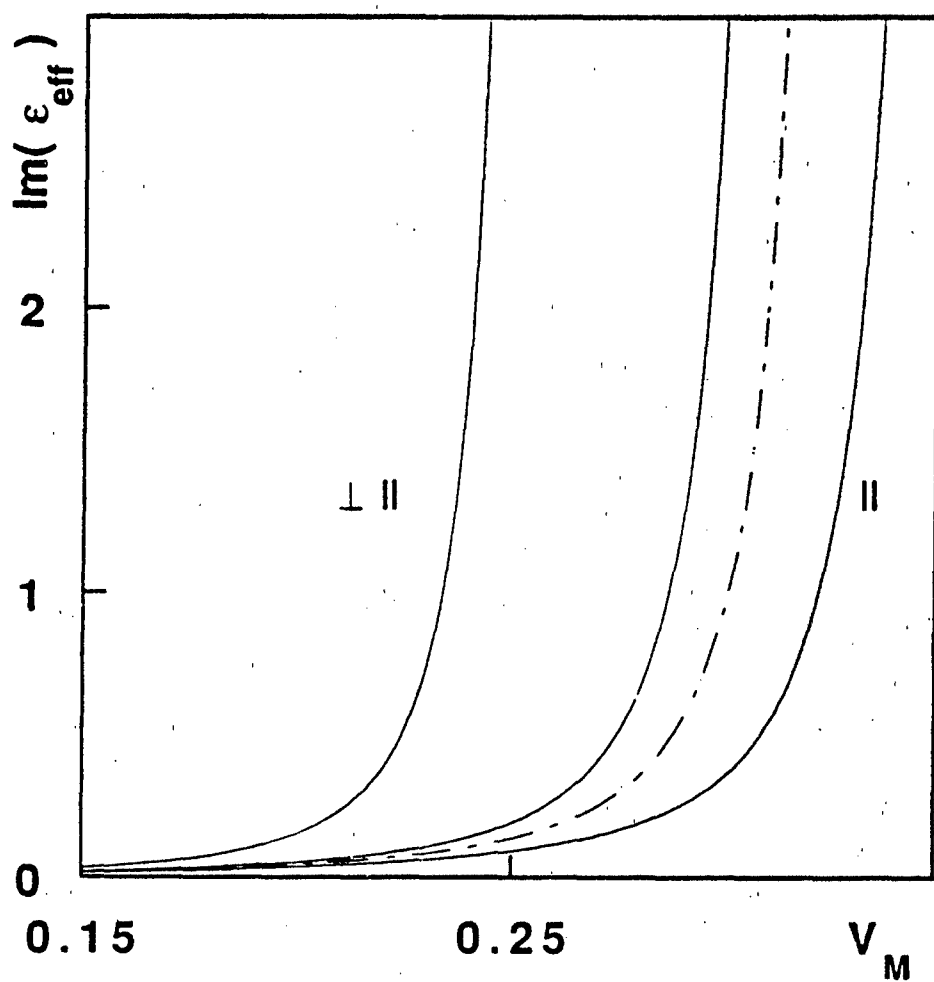


FIG. 5

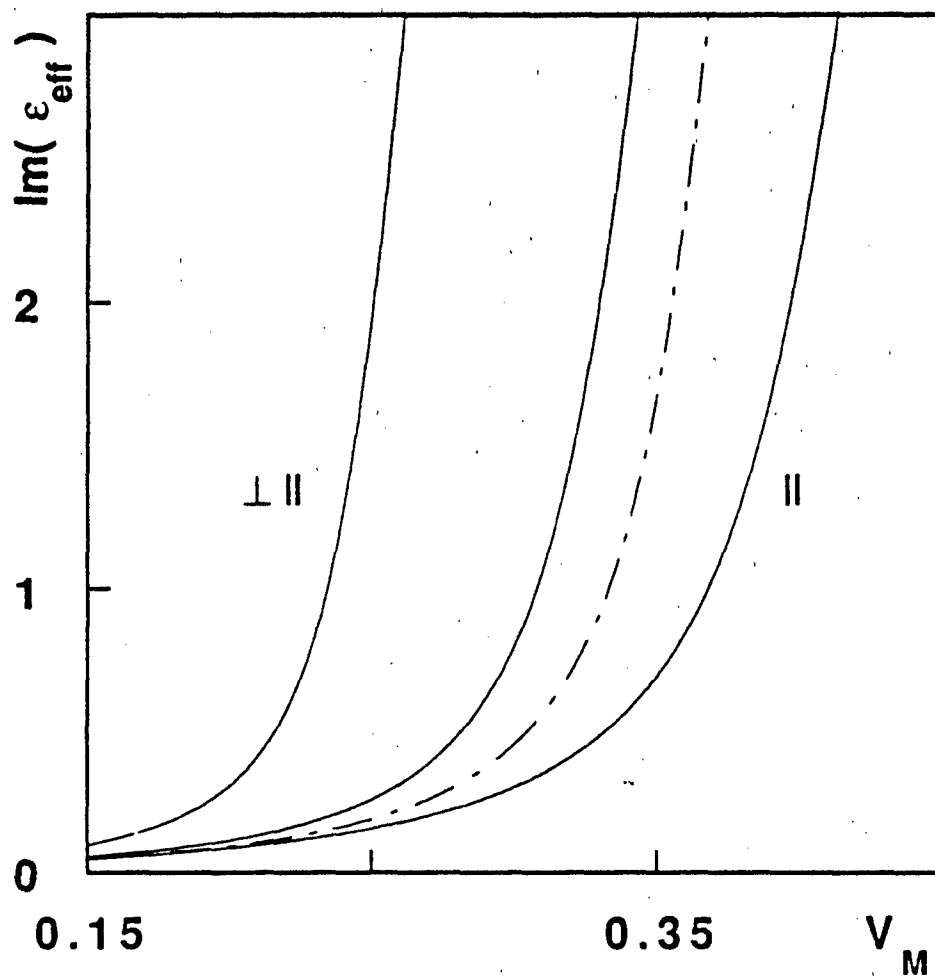


FIG. 6

PROPAGATION OF ELECTROMAGNETIC WAVES THROUGH
NON-HOMOGENEOUS MEDIA

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Abstract: The most significant results we obtained on the propagation of electromagnetic waves through non homogeneous media are summarized.

1. Introduction

A few years ago we devised a model scatterer suitable for a systematic study of the optical properties of aerosols and in particular of the effects of the anisotropy and of the possible aggregation of the constituent particles. Indeed, our model scatterer is built as a cluster of spherical objects of arbitrary radii and refractive indexes; the spheres need not be homogeneous and their relative positions are arbitrary to a large extent. The scattering of electromagnetic waves by such composite scatterers is dealt with through the use of multipole expansions to describe both the incident and the scattered field as well as the field within the component spheres [1, 2]. The resulting forward scattering amplitude has very simple transformation properties under rotation of the coordinate axes. This allows us to calculate very easily the macroscopic optical properties of a low-density dispersion of clusters even when they are randomly oriented. In fact, we are able e.g. to study the changes of the spectrum of a dispersion of spherical particles, both homogeneous and non-homogeneous [3,4], when they undergo various stages of aggregation and even when they change their mode of aggregation in, analogy to what happens in chemical reactions [5].

In the last year we started an attempt to extend our study to intermediate and high-density dispersions through a modified version of the effective medium theories [6]. Essentially the effective medium theories substitute the actual dispersion with an effective medium whose dielectric properties are calculated so as to compensate exactly for the scattering produced by the particles. Our particular work in this field consists in treating a dispersion of metal spheres with size-parameter bigger than that usually dealt with within the Bruggemann scheme [7] and yet sufficiently small to ensure the validity of the dielectric description of the medium. Accordingly we used the full Mie expansion and as a further improvement included some kind of

correlation e.g. that produced by aggregation phenomena or by an exclusion hole around each sphere. This amounts to using a mixed scheme midway between that of Bruggemann and that of Maxwell-Garnett. Some of our preliminary results will be illustrated in Section 3.

2. Theory

All the information on the propagation of electromagnetic waves through a low-density dispersion of scatterers is contained in the matrix of the refractive index [8]

$$N_{\eta\eta} = \delta_{\eta\eta} + \frac{2\pi}{Vk^2} \sum_v f_{v,\eta\eta} \quad (1)$$

where the sum runs over all the scatterers within the volume V and

$$f_{v,\eta\eta} = u_\eta^\dagger f_{v,\eta} = \frac{1}{8\pi k^2} \sum_p \exp[-ik \cdot R_v] \sum_{LM} W_{LM}^{(p)} a_{LM}^{(p)} \quad (2)$$

In eq. (2) u_η is the polarization vector and $f_{v,\eta}$ the forward-scattering amplitude of the v -th scatterer; in turn the $W_{LM}^{(p)}$'s are the multipole amplitudes of the incident plane-wave field and the $a_{LM}^{(p)}$'s are their counterparts for the scattered field. The superscript p is a parity index which distinguishes the magnetic multipole fields ($p=1$) from the electric ones ($p=2$) [9]. When the scatterer is a cluster of spheres the multipole amplitudes of the scattered field are

$$a_{LM}^{(p)} = - \sum_{L'M'} S_{LM,L'M'}^{(p)} V_{L'M'}^{(p)}$$

where the S 's are defined in ref. [3]. The most important feature of the S 's is that under rotation of the coordinate axes they transform according to the representations of the full rotation group. As a consequence, once the S 's are known for a cluster of given orientation they are immediately known for any other cluster of different orientation, and the sum in eq. (1) can be performed analytically.

For intermediate and high-density dispersions, the procedure outlined above does not yield reliable results because the multiple-scattering processes become more and more important. A possible way to overcome this difficulty is to resort to the effective medium theories such as the well-known mixing rules of Bruggeman, and of Maxwell-Garnett. The general principle on which these rules are based was outlined in sect. 1 and, as our work in the field is still in progress, we defer our further comments to the next section where some of our preliminary results will be presented.

3. Results and Discussion

Fig. 1 we report the real (1a) and the imaginary part (1b) of N_{11} for a low-density dispersion of binary clusters both oriented alike (solid lines) and at random (broken lines) versus the size parameter, $x=k\rho$, of the constituent spheres, which are homogeneous with $n=1.3$. All the curves are normalized to the corresponding quantities of a dispersion of independent spheres with the same density and refractive index and show not only a noticeable dependence on the orientation but also that for a cluster of given geometry there exist a value of the size at which this dependence disappears. Our experience suggests that this pseudo-spherical behavior is bound to appear for some value of the size when the clusters have a definite symmetry.

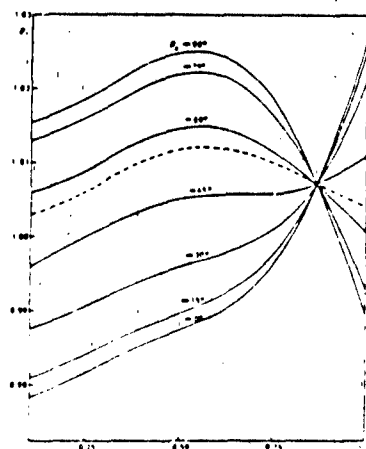


Fig. 1a

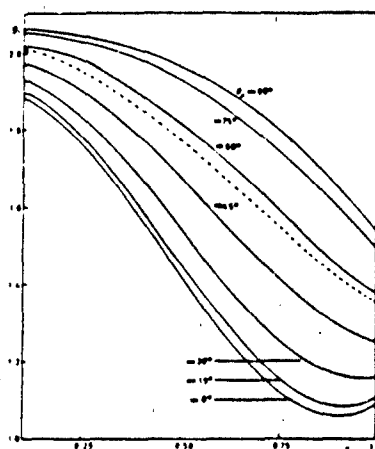


Fig. 1b

As anticipated in sect. 1, we also dealt with dispersions of layered spheres which we treated as explained in ref. [3]. In short, we kept constant the dielectric function within each layer and between each pair of them interposed a transition layer, as thin as possible, within which the radial dependence of the dielectric function is taken so as to ensure the continuity of ϵ and of its radial derivative. We considered in this way spheres with a diffuse surface, metal spheres with a dielectric or metallic coating and dielectric spheres with a metallic coating. The dielectric function of the metal was described by a free-electron Drude function, while that of the dielectric was described by a damped oscillator function. The most striking result is shown in fig. 2 which refers to spheres of MgO coated with Al with a total radius of 50 Å. It is quite evident that the absorption peaks of the dispersion of single spheres (solid lines) shift according to the thickness of the coating: thus

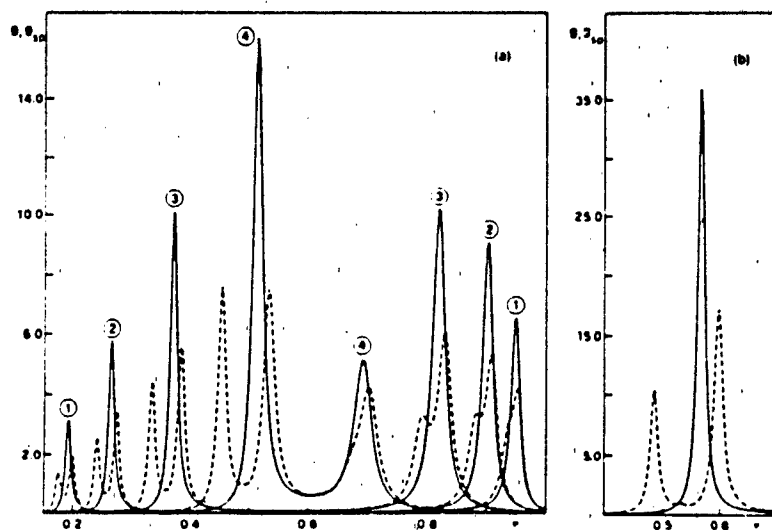


Fig. 2

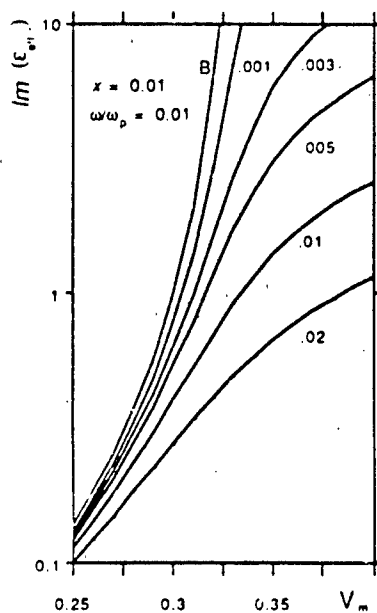


Fig. 3

this feature can be, in principle, used to obtain a selective absorption at any frequency within a given range. Nevertheless this effect can be greatly weakened if a considerable percentage of the spheres aggregate (broken lines).

At last we give here an anticipation of our present attempt to use at best the potentialities of the effective dielectric constant methods beyond the mixing rules of Bruggeman and of Maxwell-Garnett. In fig. 3 we present our results for one of the conceivable intermediate models between that of Bruggeman and that of Maxwell-Garnett. This model consists of an admixture of metal and dielectric spheres (these latter with dielectric constant $\epsilon=1$). Around each metal sphere we put a exclusion hole in the form of a layer of variable thickness with

dielectric constant $\epsilon=1$. The curves in fig. 3 are labeled by the percentage of volume occupied by the exclusion holes. The curve labelled B refers to the conventional Bruggeman rule. All the spheres were dealt with through the full Mie theory. The main result of our calculation is a dramatic shift of the percolation threshold as a consequence of the correlation of exclusion we forced on the system.

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**Computations of the Absorption Coefficient of a Dispersion of
Clusters - Comparison of Computed Data with Experimental for
Small Clusters.**

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ABSTRACT

A selection of clusters composed of 20 spheres, simulating irregularly shaped particles often observed in powders, are used to model a low density monodispersed aerosol for which the absorption coefficient is calculated. Also calculations will be shown for small clusters (composed of 2 spheres) having the same optical characteristics as those of existing experimental data with which comparison will be made.

1. Introduction.

The fact that aerosol particles, but for few exceptions, are not spherical, nor can be described as spherical in consideration of their optical properties, is well known. It is not surprising that the optical behaviour of aerosol particles as calculated using Mie Theory is seldom consistent with the experimentally observed data, since the Mie theory is based upon the sphericity of the scatterer. It is however important to achieve a reasonable confidence in solving the problem of scattering by an irregularly shaped particle. The problem is not easily solved and special difficulties arise when the scatterer is equal to or larger than the wavelength of the incident light and when the index of refraction of the surrounding medium differs more than for a small amount. We have developed a formalism which allows us to describe an irregularly shaped particle^[1-4], and the calculation of the properties

of such a complex scatterer can be performed following the approach outlined in previous works^[5-8]. Having obtained in this manner the optical properties of a single scatterer then the next step is to calculate the macroscopic optical constants for the propagation through a model aerosol. We will show that our computation for two spheres agree with experimental results^[9], then we will discuss the case of some complex structures which are types found commonly in powders^[10-12].

2. Theory.

We refer you to other papers for the details of the computations and their justifications, see^[13-17], here simply accept that we can write the extinction cross section of a whole cluster, where a cluster is the geometrical description of a particle, in the form

$$\sigma_{ext} = < V \dagger | S | V > \quad (1)$$

where the matrix S depends only on the structure of the cluster:

$$S = |I| \times |T| \times e^{i\mathbf{K} \cdot \mathbf{R}} \quad (2)$$

The matrix S includes all the information on the scattering power of the cluster as a whole (its elements depend only on the scattering power of the spheres of the cluster and on the relative positions of their centers). In eq.(2), the matrices I and T were defined previously^[7]. Matrix I has the role of referring the amplitudes of the multipole fields scattered by each sphere to the origin of the coordinates. The matrix T of the form:

$$T = \begin{vmatrix} T^{(1,1)} & T^{(2,1)} \\ T^{(1,2)} & T^{(2,2)} \end{vmatrix} \quad (3)$$

which must be calculated as the inverse of the matrix:

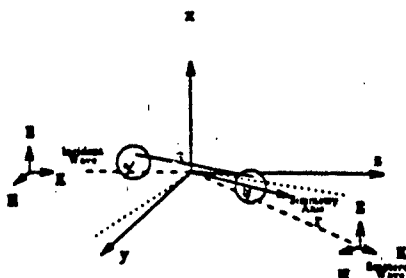
$$M = \begin{vmatrix} [R^{(1)}]^{-1} + H & K \\ I & [R^{(2)}]^{-1} + H \end{vmatrix} \quad (4)$$

and which is determined by the structure of the cluster. The matrix V represents the amplitudes of the multipole fields and its elements make eq.(1) dependent on the direction of incidence. The matrix H describes in the vicinity of the surface of each sphere the multipole fields scattered by the other spheres of the cluster. The matrix K represents the cross terms of the multipole fields. And finally the matrices $R^{(1)}$ and $R^{(2)}$ are the scattering power of the single spheres composing the cluster (identical in physical meaning to the terms A and B in Van De Hulst^[10]).

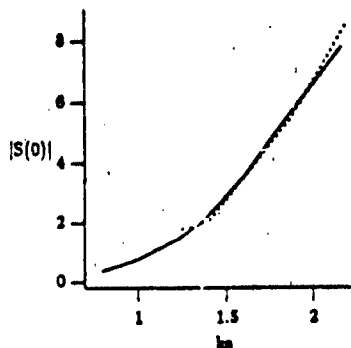
2. Results and Discussion

Two spheres — touching. The first set of data will be that of the two spheres, which will be compared with the experimental data of Shuerman and Wang^[6]. The spheres are touching, the quantities which we have computed are the complex forward scattering amplitude $|S(0)|$ as a function of the size parameter $ka = 2\pi a/\lambda$ of the cluster. The geometry and all the parameters we have used and that we report are the same as the experi-

ments for which we compare. Following we reproduce the experimental setup:



the following graph shows our calculated data (solid line) and the experimental data (dotted line).



20 Spheres. We will now consider clusters composed of 20 spheres in order to simulate some irregularly shaped aggregations often found in powders^[10-12]. In the figures we report the quantities $\Gamma = \gamma/\gamma_0$ and $\Gamma_{\perp} = \gamma_{\perp}/\gamma_0$ for several direction of incidence as a function of χ the size parameter; where γ_0 is the absorption coefficient of a dispersion of spheres of size parameter $\chi_0 = 20^{1/3} \chi$, whose number density equals that of the dispersion of clusters. The quantity γ is the absorption coefficient for the cluster randomly oriented and γ_0 depends on the orientation of the clusters with respect to the incident plane-wave. The material of the spheres composing the cluster in all cases was chosen to be homogeneous isotropic, dielectric, and nondispersive with refractive index $n=1.3$ and finally all the spheres in the clusters are identical.

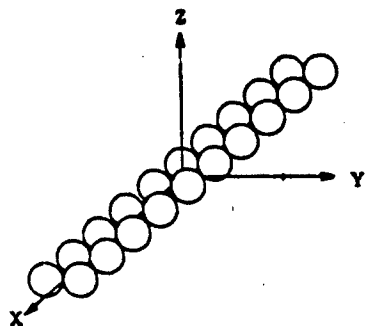


Figure 3

The cluster is defined as a *Strip* and its geometric features are shown above. In the graph below the cluster Γ (broken curve) and Γ_{θ} (solid lines) versus x for several directions of incidence for a dispersion of strips. The incident plane wave is circularly polarised. The angles of incidence (θ, ϕ), in degrees, labeling the Γ_{θ} curves are related to the common orientation of the clusters

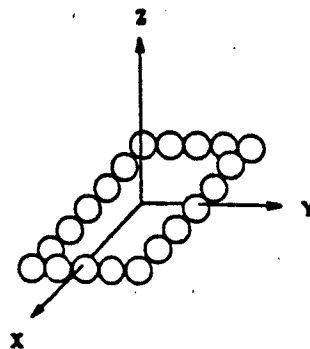
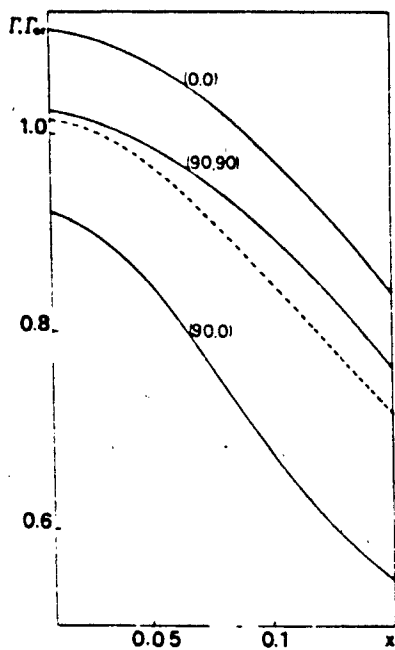
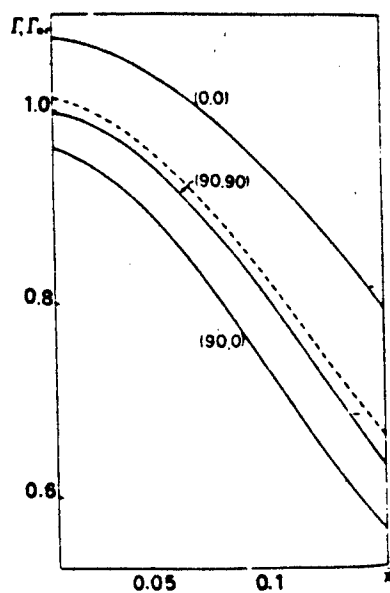


Figure 4

The cluster is defined as a *Empty rectangle* and its geometric features are shown above. In the graph below the cluster Γ (broken curve) and Γ_{θ} (solid lines) versus x for several directions of incidence for a dispersion of empty rectangles. The incident plane wave is circularly polarised. The angles of incidence (θ, ϕ), in degrees, labeling the Γ_{θ} curves are related to the common orientation of the clusters.



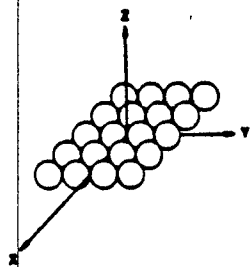


Figure 5

The cluster is defined as a *Rectangle* and its geometric features are shown above. In the graph below the cluster Γ (broken curve) and Γ_{θ} (solid lines) versus x for several directions of incidence for a dispersion of rectangles. The incident plane wave is circularly polarized. The angles of incidence (θ, ϕ), in degrees, labeling the Γ_{θ} curves are related to the common orientation of the clusters.

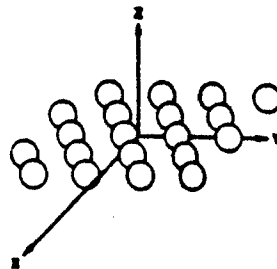
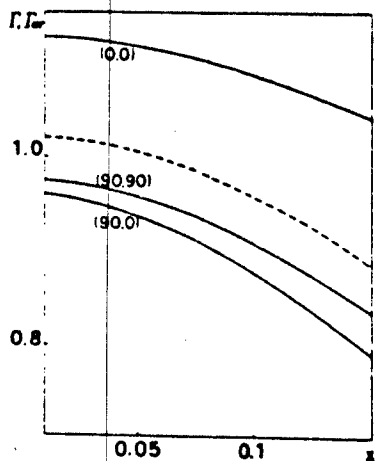
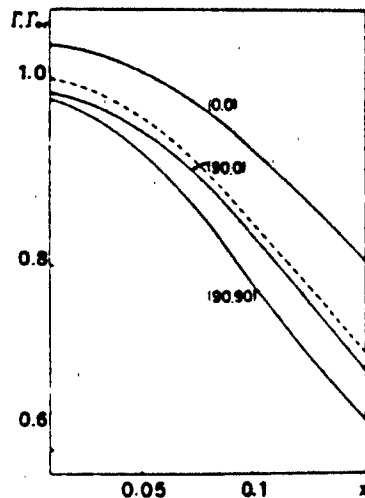


Figure 6

The cluster is defined as a *Network* and its geometric features are shown above. In the graph below the cluster Γ (broken curve) and Γ_{θ} (solid lines) versus x for several directions of incidence for a dispersion of networks. The incident plane wave is circularly polarized. The angles of incidence (θ, ϕ), in degrees, labeling the Γ_{θ} curves are related to the common orientation of the clusters.



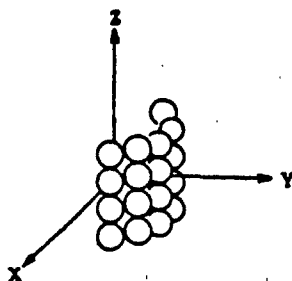


Figure 7

The cluster is defined as a *Roofing tile* and its geometric features are shown above. In the graph below the cluster Γ (broken curve) and Γ_{∞} (solid lines) versus x for several directions of incidence for a dispersion of roofing tiles. The incident plane wave is circularly polarized. The angles of incidence (θ, ϕ) , in degrees, labeling the Γ_{∞} curves are related to the common orientation of the clusters.

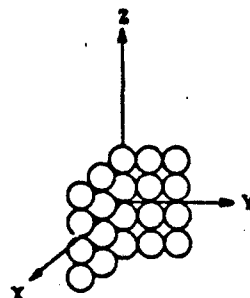
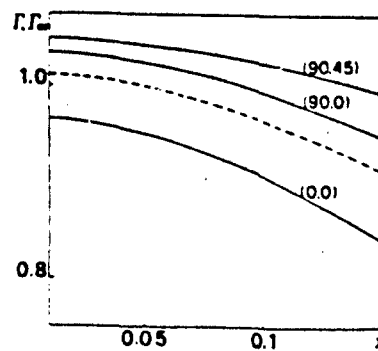
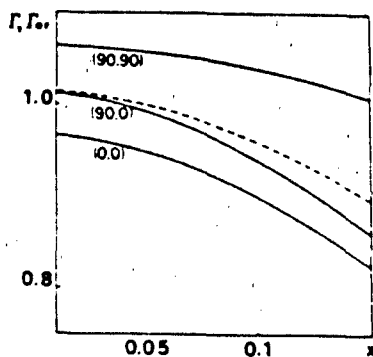


Figure 8

The cluster is defined as a *Angular strip* and its geometric features are shown above. In the graph below the cluster Γ (broken curve) and Γ_{∞} (solid lines) versus x for several directions of incidence for a dispersion of angular strips. The incident plane wave is circularly polarized. The angles of incidence (θ, ϕ) , in degrees, labeling the Γ_{∞} curves are related to the common orientation of the clusters.



On the basis of the results shown, we can conclude that the absorption efficiency of a random dispersion of identical scatterers appreciably depends on the degree of anisotropy of the single scatterers. Within large limits of the size parameter, however, several kinds of anisotropy give very similar results, as far as the compactness is comparable. Ultimately, in a random dispersion the size distribution of the scatterers as inferred from optical data should not be considered reliable if the single scatterers are appreciably anisotropic^{19,20}.

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Density dependence of the absorption coefficient of a dispersion of spherical metal particles*

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In this paper we make an attempt to assess to what extent the absorption coefficient of a dispersion of spherical scatterers is influenced by the multiple scattering effects. To this end the scatterers of the dispersion are considered as aggregated in pairs (even if they are not in contact). The field scattered by each pair is computed by means of a theory we developed in the last few years just to deal with aggregates of spherical scatterers. Of course, the field scattered by each pair depends on its orientation with respect to the incoming field as well as on the separation of the component spheres. By means of the theory cited above, we are able to sum analytically over the orientations to get the scattered field that is still a function of the distance of the spheres composing the pair. At this stage we make an weighted average over the distances using as a weight the pair correlation function for a dispersion with the density we are dealing with. As a result we get the field scattered by each sphere *dressed* by the effect of multiple scattering processes produced by the other particles. Of course this procedure yields only a first approximation as only pair effects are included while those produced by triplets and higher order multiplets of particles are neglected. We are able to show that the results we get amount to solve iteratively the exact Foldy-Twersky integral equation up to the third order iteration.

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Reliability of the theoretical description of electromagnetic scattering
from nonspherical particles.

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It is well known that the most common aerosols are composed either of irregularly-shaped particles, or of spherical particles that may undergo aggregation phenomena which in their turn give rise to effectively non isotropic compound scatterers. It is therefore not surprising that the interpretation of the optical behaviour of aerosols based on the well known Mie theory are often unsatisfactory.

A few years ago we devised a method suitable to calculate the scattering of electromagnetic waves from a cluster of spherical scatterers of known geometry. Our purpose was to account for the effect of the anisotropy of the scattering particles without undue computational effort and to see to what extent a truly irregularly-shaped particle could be approximated by a simpler system.

To describe the scattering by such a compound scatterer we make full use of the possibility of expanding both the incident and the scattered field in a series of spherical multipoles. As a consequence we are able to describe both the electric and the magnetic multipoles on the same footing without introducing any approximation but the truncation of the multipolar expansions in order to get a finite set of equations.(1).

The calculations we performed on clusters of various geometry show, as expected, a noticeable dependence on the extinction cross section (as well as of the scattering cross section) on the polarization and on the direction of incidence of the plane wave. Furthermore, thanks to the transformation properties of the spherical multipoles under rotation, we were able to show that the forward-scattering amplitude of any cluster depends analytically on the direction of incidence in a rather simple way.

All the features mentioned above are of invaluable help when comparing the results of our approach to the experimental data. Nevertheless, before we make the actual comparison with the experimental measurements of Schuerman, Wang and Greenberg(2) we recall some facts about the convergency of any calculation based on multipolar expansions.

For a single sphere, of radius b , the convergency of the calculations depends on the product $x=kb$, the so called size-parameter of the scatterer, k being the magnitude of the incident wave vector. If L_M is the maximum multipolar order entering the calculations, the convergency requires $L_M > x$. For a cluster of spheres we showed that the parameter corresponding to x is $x_0 = kb_0$, b_0 being the radius of the smaller sphere that can include the whole cluster. Even in this case a good convergency is achieved only for $L_M > x_0$. In any case scattering objects with the same x (or x_0) have the same scattering features, provided, of course, that the refractive index is non dispersive.

In figure 1 we show the experimental setup used by Schuerman and Wang to perform their measurements on single clusters as a function of the direction of incidence. We notice that to ensure the reproducibility of the results only the polarization indicated in figure 1 can be used.

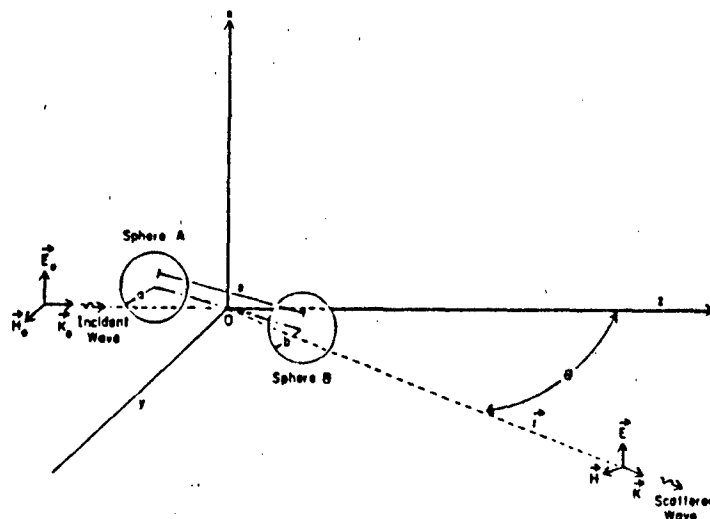
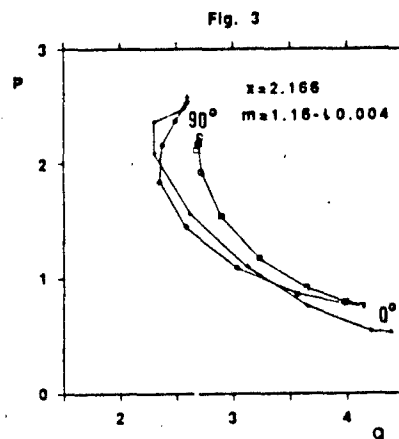
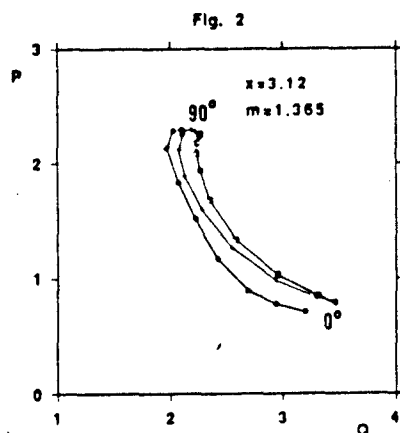


Fig. 1

In figure 2 and 3 we report the results of our calculations, for both orthogonal and parallel polarization, for a cluster of two spheres as a function of the direction of incidence, together with the corresponding experimental results of Schuerman, Wang and Greenberg(3). More precisely, on the axes are reported the real, Q , and the imaginary, P , parts of the forward scattering amplitude of the cluster.

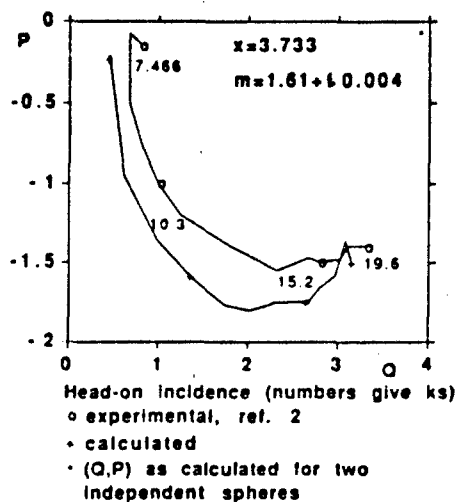


- Orthogonal polarization (experimental, ref.3)
- + Orthogonal polarization (calculated)
- Parallel polarization (calculated)

Both figure 2 and figure 3 show that the agreement between the experimental and the theoretical results is rather good. We state this also on the following considerations. First, Schuerman and Wang(3) estimate the experimental error in about 10% in magnitude and 12° in phase. Second, the angular dependence of the forward scattering amplitude can be determined analytically, and our theoretical curves are consistent with such angular dependence.

We want only to stress that according to the parameters reported in fig.2 and fig.3 the convergency of our calculations would require at least $L_M=6$. Actually we have to use $L_M=10$ for both cases. Any further increase of L_M has no effect on the results thus proving that we get the best convergence achievable through this kind of expansion of the field.

Fig. 4



In figure 4 we report the results for a cluster of two spheres whose distance is gradually increased. On account of the considerations reported above, when $x_0 \approx 15$ the convergency would require $L_M \approx 30$. This cannot be done without using delicate numerical procedures which in turn require a very large and fast computer. For this reason our present results fit satisfactorily the experimental results only for small values of x_0 , although the uncertainty of the experimental data must, even in this case, be taken into account.

In conclusion we can state that our approach is able to describe correctly the scattering from a cluster of spheres. At present we are improving the programs to include the possibility of extending the multipolar expansion to very high values of L_M . In any case both the theoretical and the experimental approach mutually support the respective findings.

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